THE

CHEMISTRY OF ESSENTIAL OILS

AND ARTIFICIAL PERFUMES

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ILLUSTRATED WITH ENGRAVINGS

LONDON

SCOTT, GREENWOOD & CO.

Publishers of the "Oil and Colourmans' Journal"

8 BROADWAY, [redacted] LUDGATE HILL, E.C.

1899

ABERDEEN UNIVERSITY PRESS

PREFACE.

THE developments in the chemistry of essential oils have been so rapid and so extensive during the past few years, that I need make no apology for the appearance of the present work, in which I have attempted to group together the more important of the published facts connected with the subject. No attempt has been made, in the chapters dealing with the preparation and analysis of essential oils, to do more than give an outline of the principles involved, as, in the first place, each subject could well occupy a volume by itself, and in the second place, no man with mere text-book knowledge would undertake either branch of the subject in a practical manner. The treatment of the essential oils systematically has necessitated the suppression of much doubtful and disputed work, and whilst great care has been taken to keep the facts up to date, it has been necessary to only touch slightly on a good deal of quite recent disputed work, which must be regarded as still in an unsettled condition.

My thanks are due to a number of friends who have rendered me much assistance during the preparation of the volume; especially to Mr. J. H. Coste, F.I.C., who has rendered much help in the

revision of the proof sheets, and Mr. H. F. Lambert, who has assisted me in the preparation of the sketches. I have also to thank the editor of the *Chemist and Druggist*, Messrs. Townson & Mercer and Messrs. Schimmel & Co., for the loan of blocks and permission to reproduce several illustrations; and Mr. Heinrich Haensel, Messrs. Stafford, Allen & Co., and Messrs. Sparks, White & Co., for generously placing numerous samples at my disposal.

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flower may be of great value in attracting the insects with the fecundating pollen, this can have no bearing on the occurrence of odorous bodies in, say, the bark or internal tissues. At present one is compelled to class the majority of the essential oils as, in general, belonging to the by-products of the metabolic processes of cell life, such as are many of the alkaloids, colouring matters and tannins; with, possibly, in certain cases, excretionary functions. The structures of the plant which carry the secreted oils occur in the fibro-vascular as well as in the fundamental tissues. Dependent on their mode of origin, the receptacles may be either closed cells containing nothing other than the matter secreted, or they may be vascular structures which have their origin in the gradual absorption of adjacent cell walls, and the consequent fusion of numerous cells into one vessel; or, again, they may be intercellular spaces, large cavities formed in two distinct ways, (1) by the decomposition of a number of adjacent cells, leaving a cavity in their place, whose origin is thus *lysigenous*, (2) by the separation of adjacent cell walls without injury to the cells themselves, thus leaving a space for the secretion, whose origin is *schizogenous*. Sometimes the oils contain a non-volatile resin in solution, forming an oleoresin. For example, isolated cells containing an oleoresin are found in some of the Laurineæ, Zingiberaceæ and Coniferæ, and intercellular spaces (the so-called *glands*) in some of the Umbelliferæ and Coniferæ.

Most of the oils occur free in the plant tissues, but occasionally they do not exist as such in the living organism, but result from the decomposition of a compound existing in the tissue, by means of a ferment in the presence of water. Examples of this are the essential oils of almond and of mustard. In the former case, the oil results from the decomposition of the glucoside amygdalin by means of the ferment emulsin, and in the latter from that of the glucoside

potassium myronate by means of myrosin, water being essential in both cases.

The physical properties of the essential oils are as varied as the sources from which they are obtained. Not only is their different nature dependent on the plant from which they are obtained, but a change of soil and climate will often

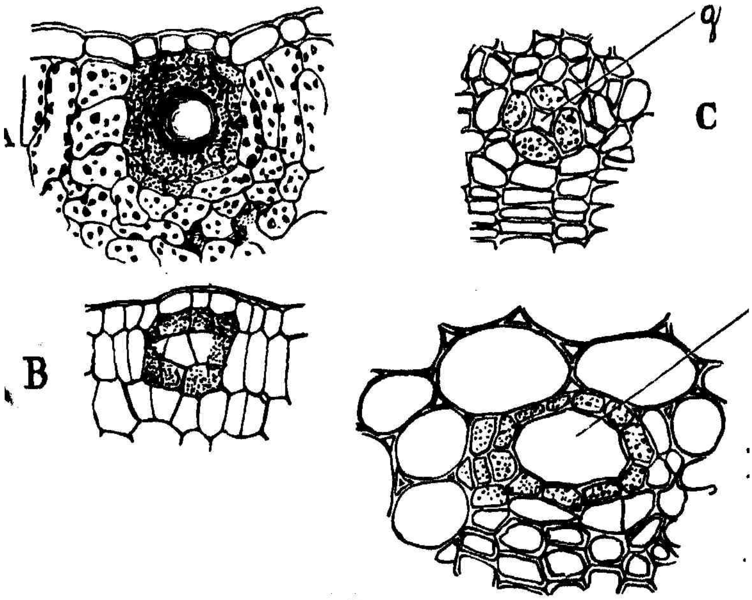


FIG. 1.

In the above diagram A represents an oil cavity below the upper surface of the leaf of *Dictamnus Fraxinella* (×320). B represents the same in an early stage, and shows the mother cells of the cavity before their absorption (lysigenous). C is an early and D a later stage of the formation of a resin passage in the young stem of the Ivy (*Hedera Helix*) (×800). In both cases *g* shows the separating cell (schizogenous).

cause enormous difference in the essential oil yielded by the same plant. Such is most markedly the case with lavender, peppermint, and roses. As an example, the first plant may be quoted. The oil distilled from plants grown at Mitcham in Surrey never contains more than about 7 to 10 per

cent. of the compound, linalyl acetate, whereas the same plant, *Lavandula vera*, growing in the south of France, frequently contains over 35 per cent. of the same body. And Mitcham plants, transplanted to the south of France, yield an oil which approximates more and more to the ordinary French oil, according to the time they have been growing under their new conditions of life.

In general, the volatile oils are practically insoluble in water, although the traces which go into solution are sufficient to render the water highly odoriferous. They are, however, soluble in most organic solvents. Their density varies from much below to much above that of water. A few consist almost entirely of one definite compound, such as oil of wintergreen, which is nearly pure methyl-salicylate, but the majority are mixtures of several different bodies. They are mostly inflammable liquids, distilling undecomposed under ordinary atmospheric pressure. A few, however, undergo some decomposition, and must be distilled under reduced pressure, or with steam. Many of them are very susceptible of change, which is chiefly brought about by oxidation by means of atmospheric air. In order to preserve such oils, they must be kept in dark, cool places, protected from the action of the air.

The optical properties of essential oils are very characteristic. They invariably possess very high refractive indices, usually from 1·45 to 1·56, and most of them have the property of rotating the plane of polarisation. The application of this property forms one of the most useful criteria in judging of the purity of a given sample of oil, and will be treated in detail in the sequel. The following table, published by Dr. Gladstone some thirty years ago (*Jour. Chem. Soc.*, xvii., p. 3), is of interest in this respect, although some of the actual figures must be rejected on account of the obvious adulteration of the samples. The rotation figures are expressed for a column of ten inches of liquid :—

Oil.	Specific Gravity at 15·5°.	Refractive Index for the D line at temperature quoted.		Rotation.
Aniseed	·9852	16·5°	1·5566	- 1°
Bay	·8808	18·5°	1·5022	- 6°
Bergamot	·8825	22°	1·4625	+ 23°
,, (Florence)	·8804	26·5°	1·4614	+ 40°
Birch bark	·9005	8°	1·4921	+ 38°
Cajuput	·9203	25·5°	1·4611	0
Caraway	·8845	19°	1·4671	+ 68°
Cassia	1·0297	19·5°	1·5748	0
Cedar	·9622	23°	1·5035	+ 3°
Citronella	·8908	21°	1·4659	- 4°
Cloves	1·0475	17°	1·5312	- 4°
Coriander	·8775	10°	1·4652	+ 21° (?)
Cubebs	·9414	10°	1·5011	—
Dill	·8922	11·5°	1·4834	+ 206°
Elder	·8584	8·5°	1·4749	+ 14·5°
Eucalyptus amygdalina	·8812	13·5°	1·4788	- 136°
,, oleosa	·9322	13·5°	1·4718	+ 4°
Indian geranium	·9043	21·5°	1·4714	- 4°
Lavender	·8903	20°	1·4648	- 20°
Lemon	·8498	16·5°	1·4727	+ 164°
Lemon grass	·8932	24°	1·4705	- 3° (?)
,, (Penang)	·8766	13·5°	1·4837	0
Mint	·9342	19°	1·4840	- 116°
,,	·9105	14·5°	1·4822	- 13°
Myrtle	·8911	14°	1·4680	+ 21°
Neroli	·8789	18°	1·4676	+ 15°
,,	·8743	10°	1·4741	+ 28°
Nutmeg	·8826	24°	1·4709	+ 44°
,, (Penang)	·9069	16°	1·4818	+ 9°
Orange peel	·8509	20°	1·4699	+ 32° (?)
,, (Florence)	·8864	20°	1·4774	+ 216°
Parsley	·9926	8·5°	1·5162	- 9°
Patchouli	·9554	21·°	1·5050	—
,, (Penang)	·9592	21°	1·5040	- 120°
,, (French)	1·0119	14°	1·5132	—
Peppermint	·9028	14·5°	1·4670	- 72°
Petitgrain	·8765	21°	1·4600	+ 26°
Rose	·8912	25°	1·4627	- 7°
Rosemary	·9080	16·5°	1·4688	- 17°
Sandalwood	·9750	24°	1·5021	- 50°
Thyme	·8843	19°	1·4754	—
Turpentine	·8727	13°	1·4732	- 79°
Verbena	·8812	20°	1·4870	- 6°
Wintergreen	1·1423	15°	1·5278	+ 8°
Wormwood	·9122	18°	1·4688	—

The composition of the essential oils is as variable as are their physical properties, and the next chapter will be devoted to a study of the more important groups of chemical compounds which occur in them. Many of them contain

several liquid ingredients, but some are solutions of solid bodies in liquids. These will frequently deposit the greater portion of the solid on being exposed to a low temperature. When this is the case, the solid is frequently referred to as the *stearoptene*, and the liquid as the *eleoptene*. These terms, however, have now no scientific meaning. After these introductory remarks we may now pass on to a detailed account of the more commonly occurring compounds in the essential oils, and thence to a study of the special oils themselves.

CHAPTER II.

COMPOUNDS OCCURRING IN ESSENTIAL OILS.

THE old terms *fatty* and *aromatic* as applied to chemical compounds have gradually given way to the more scientifically correct *open chain* and *closed chain*, as it has been found that many of the highly odoriferous bodies do not belong to the benzene series of compounds. The bodies described here will therefore be classified according to their possessing a closed carbon chain in the molecule or not. The groups whose members are frequent constituents of essential oils are: (1) the terpenes, (2) camphor compounds, (3) the geraniol series, (4) benzene compounds, (5) open chain or aliphatic compounds other than (3).

I. THE TERPENES.

No compounds are of more frequent occurrence in essential oils than are those belonging to this important group. Very many have been described by different chemists, but a systematic study undertaken by Wallach has reduced these to a comparatively few, the best defined of which are those described below. They are, with one exception, volatile liquid hydrocarbons of the formula $C_{10}H_{16}$. Whilst agreeing closely in many of their properties, their chemical differences are sufficient to enable them to be sharply differentiated. The well-defined terpenes are: *pinene, camphene, limonene, dipentene, fenchene, sylvestrene, carvestrene, phellandrene, terpinolene, terpinene*, and *thujene*.

Pinene.—This hydrocarbon occurs in both the dextro- and the laevo-rotary form in nature. It has been described at various times as *terebenthene*, *australene*, *eucalyptene*, *laurene*, *olibene* and *massoyene*, all of which, however, were more or less impure pinene.

The active varieties of pinene are prepared by fractional distillation of a number of essential oils. American turpentine is the chief source of dextro-pinene, and French turpentine of laevo-pinene. Optically inactive pinene does not occur in nature, but can be prepared by heating pinene nitrosochloride with aniline. Its properties, according to Wallach (*Ann. Chem.*, cclii., p. 132, and cclviii., p. 343), are as follows: an optically inactive liquid, boiling at 155° to 156°, of specific gravity ·858 at 20°; refractive index for the *d* line 1·4655 at 21°. The purest forms of active pinene prepared agree closely in their properties with the above, except that their optical activity is about + 40° or − 40°. When acted upon by hydrochloric acid gas, pinene yields a monohydrochloride $C_{10}H_{16}HCl$, in crystals melting at 125°, known as artificial camphor. It is extraordinary that the hydrochloride prepared from *dextro*-pinene is *inactive* (*Gazz. Chim.*, 1888, p. 223), whilst that from *laevo*-pinene is strongly laevo-rotary. By abstracting the molecule of hydrochloric acid, by means of sodium acetate and acetic acid, the hydrocarbon recovered is not pinene, but camphene. The further action of hydrochloric acid on pinene results in the formation of dipentene dihydrochloride, showing that a molecular re-arrangement has taken place. Pinene yields a characteristic compound with nitrosylchloride, $C_{10}H_{16}NOCl$, which is of great use in identifying the hydrocarbon. It is best prepared (*Ann. Chem.*, ccliii., p. 251) by adding 15 c.c. of fuming hydrochloric acid to a well-cooled mixture of 50 c.c. each of turpentine, glacial acetic acid, and ethyl nitrite. The nitrosochloride separates as a crystalline precipitate, and can be washed with alcohol to purify it. It

then melts at 103° and is optically inactive. By the action of alcoholic solutions of various amines on the nitrosochloride, characteristic nitrolamines are formed, of the general formula

$$C_{10}H_{16}\begin{matrix} \diagup NO \\ \diagdown NHR \end{matrix}$$

where R is the amine radicle. Of these pinene nitrol-piperidine melts at 118° and pinene nitrol-benzylamine at 122°. By treating pinene nitrosochloride with alcoholic potash nitroso-pinene $C_{10}H_{15}NO$ is obtained. This body forms monoclinic crystals melting at 132°. The action of bromine on pinene gives rise to a solid di-bromide $C_{10}H_{16}Br_2$ melting at 169°, and possibly to a liquid tetrabromide.

The exact constitution of pinene is still a matter of doubt, but the most probable formula for this, and those for several of the other terpenes, are given below.

Camphene.—This is the only solid terpene known. It occurs to a small extent in a few essential oils, such as citronella, ginger and camphor oils. It is prepared artificially, however, by several reactions, such, for example, as that mentioned above, *viz.*, the withdrawal of HCl from pinene monohydrochloride, or by the action of heat in the presence of acetic anhydride on bornylamine, $C_{10}H_{17}NH_2$, which causes the withdrawal of ammonia and leaves camphene, as follows:—

$$C_{10}H_{17}NH_2 = C_{10}H_{16} + NH_3.$$

Camphene is a crystalline body, melting, according to Wallach, at 48° to 49°, according to Brühl, at 51° to 54°. It boils at about 160°. It is known in the inactive, as well as in the dextro- and laevo-rotary forms. A sample prepared by Bouchardat (*Comptes rendus*, civ., p. 693) was laevo-rotary $[a]_d = -80·6°$. The compounds of camphene are less stable than those of pinene, and have not, in most cases, been prepared in a pure state.

Limonene.—This terpene is one of the most important, as it forms from 80 to 90 per cent. of several essential oils. It is known in the dextro- and laevo-rotary forms, whilst when inactive it is known as dipentene, which will be discussed separately. This hydrocarbon has been described under the names hesperidene, citrene, carvene, etc. It occurs as dextro-limonene in oils of lemon, orange, bergamot, dill and other oils, and as laevo-limonene in certain pine needle oils, and Russian peppermint oil. It is a liquid of specific gravity ·846 at 20°, boiling at 175° to 176°, of refractive index 1·4746. The purest samples of dextro- and laevo-limonene prepared had for their optical activity − 105° and + 106·8° respectively (*Ann. Chem.*, cclii., p. 144). With hydrochloric acid limonene yields an optically active monohydrochloride, but in the presence of water dipentene dihydrochloride is formed. By the action of bromine, a tetrabromide $C_{10}H_{16}Br_4$ is formed, which melts at 104°, and is a very useful body for identifying the hydrocarbon. Both limonenes yield nitrosochlorides $C_{10}H_{16}NOCl$, each of which can be separated into two modifications. Here as in every other case, the only difference between the derivatives of the two limonenes is that they are equally active optically in the opposite directions, and differ in the usual way in crystalline form. The nitrosochlorides, on boiling with alcoholic potash, yield nitroso-limonenes $C_{10}H_{15}NO$. These are identical with the two carvoximes, and their constitution is probably $C_{10}H_{14}.NOH$. They both melt at 72°. The carvoxime prepared from *dextro*-limonene-nitrosochloride is *laevo*-rotary, whilst that from *laevo*-limonene-nitrosochloride is *dextro*-rotary. The following experimental determinations show how closely the optical activities of the various limonene derivatives agree. Theoretically they should of course be exactly equal.

Compound.	Prepared from	
	Dextro-limonene.	Laevo-limonene.
Limonene	+106·8°	−105°
Tetrabromide	+73·3°	−73·4°
Nitrosochloride	+313·4°	−314·8°
Carvoxime	−39·3°	+39·7°
Nitrolbenzylamine	+163·8°	−163·6°
Monohydrochloride	−40°	+39·5°

Dipentene.—This hydrocarbon was for some time regarded as a distinct individual, but it is now known that, although it is such in a sense, it is the optically inactive form of limonene. The limonenes bear to dipentene the same relationship as do the optically active tartaric acids to racemic acid. Dipentene occurs in several essential oils, for example, in camphor oil, in certain turpentine oils, in cubeb oil, and in thyme oil. It also results from the isomerisation of several other terpenes by means of heat, or by mixing equal quantities of the two active limonenes. To obtain it in a state of purity, however, the best method is to boil dipentene dihydrochloride with an equal weight of dry sodium acetate and two parts of acetic acid for half an hour under a reflux condenser. The resulting oil is steam distilled, boiled with potash, and again distilled with steam and purified by fractional distillation.

It has often been stated that dipentene boils at a much higher temperature than limonene. This, however, is not so, and, doubtless, the examination of impure samples is responsible for this statement. Pure dipentene boils at about 178°, and has a specific gravity ·845 at 20°, and a refractive index 1·47308. The relationship of dipentene to limonene is here indicated, and is proved by the fact that its derivatives can, without exception, be prepared by mixing equal quantities of the same derivatives of the two limonenes.

The following are amongst the most important of its derivatives. Dipentene dihydrochloride $C_{10}H_{16}.2HCl$ is formed by the action of gaseous hydrochloric acid on either dipentene, pinene or limonene. It forms crystals, melting at 50°, and boils at 118° to 120° under a pressure of 10 mm. The tetrabromide $C_{10}H_{16}Br_4$ is a useful body for identifying the terpene. It is prepared by the action of bromine on dipentene, and when pure melts at 125° to 126° (the limonene tetrabromides, which melt at 104°, yield this body when mixed in equal quantities). The nitrosochloride is quite analogous to the above-mentioned bodies. It occurs in two modifications. The action of alcoholic potash solution on this body gives the inactive nitroso-dipentene, which is identical in every respect with inactive carvoxime, melting at 93°.

Fenchene.—This terpene is not found in nature, or if so, only to a very minute extent. It may be prepared by reducing the ketone, fenchone $C_{10}H_{16}O$ to its alcohol fenchyl alcohol $C_{10}H_{17}OH$, from which the elements of water can be separated by means of potassium bisulphate at a high temperature, when fenchene $C_{10}H_{16}$ results. It is an optically inactive hydrocarbon, of specific gravity ·864, and refractive index 1·4690. It boils at 158° to 160°. It combines with two atoms of bromine, yielding a liquid dibromide, which has not yet been obtained in a pure state. Fenchene is a stable terpene, resisting the action of nitric acid in the cold to a much greater extent than other terpenes.

Sylvestrene.—This terpene occurs in Swedish and Russian oils of turpentine and various pine oils. It can be prepared, according to Wallach (*Ann. Chem.*, ccxxxix., p. 24), by diluting with an equal volume of ether the fraction of Swedish turpentine which boils between 174° and 178°. This is saturated with dry hydrochloric acid gas, and, after allowing the whole to stand for two days, the ether is distilled off, and the residue

crystallises. By recrystallisation from warm alcohol it can be obtained pure, when it melts at 72°. The hydrocarbon is obtained from its dihydrochloride by heating with aniline, or with acetic acid and sodium acetate. Sylvestrene has an odour recalling that of bergamot. It boils at 176° to 177°, has a specific gravity ·851 at 15·5°, and a refractive index 1·4747. Natural sylvestrene is dextro-rotary $[\alpha]_d = + 66·3°$. A characteristic colour reaction of this terpene is as follows: one drop of sylvestrene is dissolved in a little acetic anhydride, and one drop of concentrated sulphuric acid is added. An intense blue colour results. It is a most stable terpene, which polymerises under the influence of heat, without yielding any of the isomeric terpenes. It forms a characteristic dihydrochloride, already mentioned, and a tetrabromide $C_{10}H_{16}Br_4$, melting at 135°. The nitrosochloride melts at 106° to 107°. The various compounds of sylvestrene which have been prepared are, as is the hydrocarbon, dextro-rotary.

Carvestrene.—This hydrocarbon is, in all probability, the optically inactive variety of sylvestrene. But this cannot be definitely proved until it is resolved into the two optically active varieties, or until laevo-sylvestrene is discovered, when a mixture of the two sylvestrenes should yield carvestrene. It yields the characteristic sylvestrene colour reaction mentioned above, which the other terpenes do not. Carvestrene has not been found in nature, having been prepared by Baeyer (*Berichte*, xxvii., p. 3485) by the distillation of carylamine hydrochloride, $C_{10}H_{17}NH_2 . HCl$, in an atmosphere of dry hydrochloric acid gas. It is an optically inactive liquid, boiling at 178°. It forms a crystalline dihydrochloride, $C_{10}H_{16}$ 2HCl, melting at 52·5°, and a dihydrobromide melting at 49°.

Phellandrene.—This terpene, which derives its name from the plant *Phellandrium aquaticum* (water fennel), is

found in both the dextro- and the laevo-rotary forms in several essential oils. The fennel oils contain *dextro*-phellandrene, whilst the *laevo-* variety is found in the oil of *Eucalyptus amygdalina* and other oils. The hydrocarbon boils at about 170°, and has a specific gravity ·8558 at 10°, and a rotation of about 18°. It is an unstable terpene, easily susceptible of isomeric change. Its most characteristic derivative is the nitrite $C_{10}H_{16}N_2O_3$. This is prepared by adding 5 grammes of sodium nitrite in 8 c.c. of water to 5 c.c. of the phellandrene-containing fraction of an oil, previously dissolved in 10 c.c. of petroleum ether, and well shaken; 5 c.c. of acetic acid are then added. The resulting crystals are washed with water and alcohol, and finally dissolved in chloroform, from which the pure body is precipitated by the addition of alcohol. The nitrite prepared from dextro-phellandrene is laevo-rotary, and *vice versâ* (*Gazz. Chim.*, xvi., 225). The specific rotation is 183·5°, and the crystals melt at 103°. Constitutionally, there is no doubt that phellandrene is closely related to carvone.

Terpinolene.—This terpene has not been found in nature. It is formed by the isomerisation of other terpenes by the action of sulphuric acid, or by heating cineol or terpineol with sulphuric or phosphoric acid. It is known only in the optically inactive variety. It boils at about 188°, and has a specific gravity of about ·855. It forms a well-defined dibromide melting at 69°, and a tetrabromide melting at 116°.

Terpinene.—This terpene was found by Weber in oil of cardamoms (*Ann. Chem.*, ccxxxviii., p. 107). It results, like terpinolene, from the isomerisation of several of the other terpenes by the action of sulphuric acid. It boils at about 180°, and has a specific gravity ·847 at 20°, and a refractive index 1·48458. It is optically inactive. It forms a nitrosite $C_{10}H_{16}N_2O_3$ melting at 155°. The halogen addition products are liquid.

Thujene.—This hydrocarbon has not, so far, been found in nature. It has been prepared by distilling thujylamine hydrochloride, a base prepared from the ketone thujone, which occurs in oil of thuja. It was formerly described by Semmler under the name of tanacetene, when he prepared it from one of the constituents of oil of Tansy. Thujene boils at 172°, and has a specific gravity of about ·840, and a refractive index 1·47145.

The sesquiterpenes are polymers of the terpenes, with which they are closely related, of the formula $C_{15}H_{24}$. A large number no doubt exist, but on account of the difficulty in purifying the hydrocarbons none can be said to be established as definite individuals until pure derivatives are prepared, whose properties can be studied. The well-defined sesquiterpenes appear to be the following: *cadinene, caryophyllene, cedrene, clovene, humulene, ledene, patchoulene,* and a hydrocarbon occurring in the oil of *Cannabis indica.*

Cadinene.—This sesquiterpene is found in the oils of cade, patchouli, galbanum and others. To prepare it in the pure state, Wallach recommends the following process. The fraction of oil of cade boiling between 260° and 280° is saturated with hydrochloric acid gas, and the resulting cadinene hydrochloride is purified and re-converted into the hydrocarbon by heating it with aniline. When pure, cadinene boils at 275°, and has a specific gravity ·921 at 15·5°, and a refractive index 1·5065. It is laevo-rotary $[\alpha]_d = -98·6°$. It forms a dihydrochloride, melting at 117° to 118°, of the formula $C_{15}H_{24}2HCl$, and corresponding compounds with hydrobromic and hydriodic acids. All these compounds are laevo-rotary.

Caryophyllene.—It is doubtful whether this body has yet been prepared in a state of absolute purity. It was first characterised as a definite sesquiterpene by Wallach, who converted it into a crystalline alcohol, caryophyllene alcohol.

The purest caryophyllene obtained from clove oil, in which it occurs to a considerable extent, had the following characteristics: boiling point, 259°; specific gravity at 15° ·9085; refractive index, 1·5009. It was optically inactive. The compounds of this sesquiterpene with the halogen acids are fluid, but a *solid nitrosochloride*, $C_{15}H_{24}NOCl$ exists, melting at 162°. The nitrosate, $C_{15}H_{24}N_2O_4$, crystallises in needles, melting at 148°. To prepare the crystalline alcohol, 25 grammes of crude caryophyllene (obtained from oil of cloves by distillation, or by absorbing the eugenol with solution of caustic alkali) are added to a mixture of 1000 grammes of acetic acid, 20 grammes of concentrated sulphuric acid, and 40 grammes of water. This is heated for several hours in the water bath. The product of the reaction is distilled with steam, when, during the latter part of the process, the solid alcohol distils over. This is separated and dried, and finally re-distilled. The alcohol, $C_{15}H_{25}OH$, boils at 288°, and sublimes in needles, melting at 95°. It is almost insoluble in water, but soluble in the usual organic liquids. It is optically inactive. It is characterised by the formation of a phenylurethane, $C_{15}H_{25}O . CO . NH . C_6H_5$, melting at 136°. It also forms an acetate, $C_{15}H_{25}O . COCH_3$.

Cedrene is the characteristic sesquiterpene of cedar wood oil. Its properties are, however, not yet definitely agreed upon, as it is doubtful whether it has been prepared in a pure state. According to Rousset (*Bull. Soc. Chim.*, 1897, p. 485) its optical activity is −47·9°, whilst other chemists give it as −60°. Its specific gravity is about ·936. Chapoteaut has alleged that the hydrocarbon of cedar wood oil has the formula $C_{15}H_{22}$, and that it is identical with that yielded by the action of phosphoric anhydride on santalal, one of the constituents of santal wood oil. This sesquiterpene greatly needs investigation.

Clovene.—This hydrocarbon has not been found in nature. When caryophyllene alcohol is treated with dehydrating agents, it yields up water, with the formation of a hydrocarbon which is not identical with caryophyllene. This is termed clovene. Its boiling point is nearly identical with that of caryophyllene, *viz.*, 262°, but its specific gravity is ·930 at 18°. It is further distinguished from the hydrocarbon to which it owes its existence by not yielding a crystalline alcohol, when treated in the way described for obtaining caryophyllene alcohol from caryophyllene.

Humulene.—This hydrocarbon was discovered in oil of hops by Chapman (*Jour. Chem. Soc.*, 1895, p. 54). It is a liquid boiling at 265°, under ordinary pressure, and of specific gravity ·9001. It forms liquid halogen compounds, and does not yield a crystalline alcohol. The nitrosochloride, however, $C_{15}H_{24}NOCl$, is crystalline, and melts at 164°. The nitrosate, $C_{15}H_{24}N_2O_4$, melts at 162°.

Ledene.—This sesquiterpene has not been found naturally, it having been prepared by dehydrating ledum camphor $C_{15}H_{26}O$ (from *Ledum palustre*). It boils at 255°, but its properties are not well understood.

Patchoulene.—This, too, is obtained by dehydrating its corresponding alcohol, the so-called patchouli camphor $C_{15}H_{26}O$. It boils at 254°, has a specific gravity ·939 at 23°, and a refractive index 1·50094. It closely resembles cedar in odour.

Sesquiterpene from Oil of Cannabis Indica.—This may fairly be considered a definite body, as it has been isolated by many different observers and described by them at different times. Valenta (*Gazzetta*, 1880, p. 540) first mentions it. Vignolo (*Gazzetta*, 1895, p. 110) describes it as a mobile liquid boiling at 256°, of specific gravity ·897 at 15°, and slightly laevo-rotary. Wood, Spivey and Easterfield (*Jour. Chem. Soc.*, 1896, p. 543) give the boiling point as 258° to 259°, the

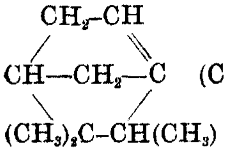
Compound.	Boiling point.	Sp. Gr. at 15·5°.	Optical rotation.	Hydrochloride melting point.		Bromide melting point.		Nitroso-chloride.		Nitroso-compound.		Nitrite.		Remarks.
				Mono-	Di-	Di-	Tetra-	Melting point.	Rotation.	Melting point.	Rotation.	Melting point.	Rotation.	
Pinene . .	155°-156°	·861	±40°	125°	—	169°	—	103°	0°	132°	0°	—	—	
Camphene .	160°	·850(at 50°)	±80°	—	—	—	—	—	—	—	—	—	—	
Limonene .	175°-176°	·848	±106°	—	—	—	104°	103°	±314°	72°	±39·5°	—	—	Figures for nitrosochloride are for the a variety. Rotations of the nitroso-compounds are of opposite sign to those of the terpenes.
Dipentene .	178°	·848	0°	—	50°	—	125°	103°	0°	93°	0°	—	—	
Fenchene .	159°	·864	0°	—	—	—	—	—	—	—	—	—	—	
Sylvestrene .	176°	·851	+66·3°	—	72°	—	135°	106°	—	—	—	—	—	
Carvestrene .	178°	—	0°	—	52·5°	—	—	—	—	—	—	—	—	
Phellandrene	170°	·853	±18°	—	—	—	—	—	—	—	—	103°	±183·5°	Rotation of nitrite is of opposite sign to the terpene.
Terpinolene .	185°-190°	·855	0°	—	—	69°	116°	—	—	—	—	—	—	
Terpinene .	180°	·849	0°	—	—	—	—	—	—	—	—	155°*	—	* Nitrosite.
Thujene .	172°	·840	—	—	—	—	—	—	—	—	—	—	—	
Cadinene .	275°	·921	-98·6°	—	117°	—	—	—	—	—	—	—	—	
Caryophyllene	259°	·909	0°	—	—	—	—	162°	—	—	—	148°*	—	* Nitrosate $C_{15}H_{24}N_2O_4$. Yields a solid alcohol melting at 95°, $C_{15}H_{25}OH$.
Clovene . .	262°	·932	0°	—	—	—	—	—	—	—	—	—	—	
Cedrene .	261°	·936	-48°	—	—	—	—	—	—	—	—	—	—	
Humulene .	265°	·900	-·5°	—	—	—	—	164°	—	—	—	162°*	—	* Nitrosate.
Ledene . .	255°	—	—	—	—	—	—	—	—	—	—	—	—	
Patchoulene .	254°	·939	—	—	—	—	—	—	—	—	—	—	—	
Cannibene (?)	258°	·897	-9°	—	—	—	—	—	—	—	—	—	—	

specific gravity as ·898 at 18°, and the rotation as $-8·6°$. The name *cannibene* may be applied to this hydrocarbon. Personne first gave this name to what is now known to be an impure compound obtained from the oil.

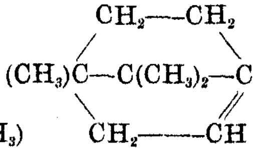
There have been numerous other sesquiterpenes described, but they have always been prepared in a doubtful state of purity. But little information is given of their properties, and less of their derivatives. There is no doubt that a closer examination of these will establish the chemical individuality of some, but will prove that many are but impure forms of bodies already known and described. An extensive and systematic study of this complex group of bodies is very urgently needed. The foregoing table summarises the chief physical characters of the well-known terpenes and sesquiterpenes. Many of them are necessarily only approximate.

The following diagrammatic formulæ are amongst the most probable of those which have been put forward as representing the constitution of several of the terpenes. Two remarks, however, must be made in this connection. The instability of this group of bodies, and the ease with which they enter into reaction, are such as to have so far prevented their constitution being settled at all definitely. Secondly, so many different views are held on the matter, that those formulæ only which appear to the author to have most in their favour have been selected, and the names of their authors are appended.

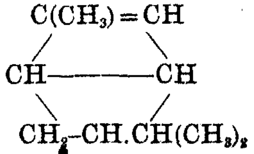
PINENE.



Tiemann.

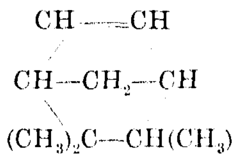


Bredt.

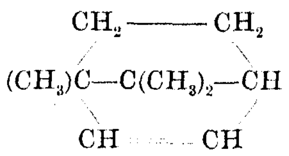


Wallach.

CAMPHENE.

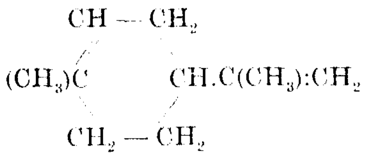


Tiemann.



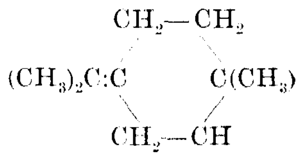
Bredt.

LIMONENE AND DIPENTENE.



Tiemann and Semmler.

TERPINOLENE.



Baeyer.

II. THE CAMPHOR SERIES.

Under this heading may be classed a number of oxygenated compounds which are closely related in their chemical constitution to the terpenes. The more important of these may be grouped in pairs—an alcohol with its corresponding ketone. A few other bodies than these will be described here, chiefly as a matter of convenience. The following, then, are the most important, and better known of these bodies :—

Alcohols.			*Ketones.*
Borneol,	$C_{10}H_{17}OH$	. .	Camphor, $C_{10}H_{16}O$.
Isoborneol,	$C_{10}H_{17}OH$	. .	—
Fenchyl alcohol,	$C_{10}H_{17}OH$	. .	Fenchone, $C_{10}H_{16}O$.
Thujyl alcohol,	$C_{10}H_{17}OH$	. .	Thujone, $C_{10}H_{16}O$.
Terpineol,	$C_{10}H_{17}OH$	. .	—
Pulegol,	$C_{10}H_{17}OH$	. .	Pulegone, $C_{10}H_{16}O$.
Menthol,	$C_{10}H_{19}OH$	. .	Menthone, $C_{10}H_{18}O$.

Borneol, $C_{10}H_{17}OH$.—This compound occurs naturally, in both optically active modifications; as dextro-borneol in the wood of *Dryobalanops camphora* (Borneo camphor), and as laevo-borneol in *Blumea balsamifera* (Ngai camphor). It

also occurs optically inactive. It forms crystalline masses, or, when recrystallised from petroleum ether, fine tablets which, when quite pure, melt at 203°. Its boiling point is only a few degrees higher, *viz.*, 212°. According to Bouchardat the melting point is lower than that given, but this is undoubtedly due to the fact that his borneol was impure, probably containing some isoborneol. Borneol can be *prepared artificially* by reducing its ketone (camphor) with sodium. Fifty grammes of pure camphor are dissolved in 500 c.c. of nearly absolute alcohol, and treated with 60 grammes of sodium. After the reaction is complete the whole is poured into a large volume of water, and the resulting borneol is collected, washed, pressed and recrystallised from petroleum ether. This method of preparation, however, yields a mixture of borneol and isoborneol. The chemically pure body is best prepared by the saponification of its acetate. On oxidation, the converse reaction takes place, with the formation of camphor. Borneol forms a series of esters with the organic acids, of which bornyl acetate is most frequently found in nature. This body melts at 29°, and has a specific gravity of ·991 at 15°. It is optically active. In common with a large number of alcoholic bodies it forms a crystalline phenylurethane. This can be prepared by the interaction of phenylcyanate and borneol. It melts at 138°. Bornyl chloride, prepared by the action of phosphorus pentachloride on borneol, melts at 157°.

Borneol forms crystalline compounds with chloral and bromal, the former melting at 55° and the latter at 98°.

The remarks made under camphor as to its probable constitution apply to borneol, remembering that the two bodies are related to one another as an alcohol and ketone.

Isoborneol.—This alcohol is isomeric with borneol, which it closely resembles. In the opinion of Jünger, the two bodies are geometrical isomerides of otherwise identical

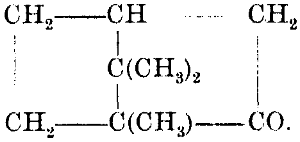
chemical structure. Isoborneol is obtained together with borneol, when camphor is reduced with sodium, and also by hydrating the terpene, camphene, by means of acetic and sulphuric acid (*Jour. prakt. Chem.*, xlix., p. 1). When isoborneol is heated with zinc chloride it yields camphene, whereas borneol, under the same treatment, remains unaltered. This renders Jünger's theory of the isomerism of the two bodies somewhat doubtful. The compounds of isoborneol are analogous in every respect to those of borneol. The following table, compiled from Heusler's *Die Terpene*, gives a comparison of some of their properties :—

	Borneol.	*Isoborneol.*
Melting point . . .	203° . .	212°.
Boiling point . . .	212° . .	Undetermined.
Specific rotation (approximate)	35° . .	4°.
Phenylurethane . .	Melts at 138°	Melts at 138°.
Chloral compound . .	Melts at 55°	Liquid.
Acetic ester . . .	Melts at 29°	Liquid.
Behaviour with zinc chloride	Unaltered .	Yields camphene.

Camphor, $C_{10}H_{16}O$.—This body occurs in the wood of the camphor tree (*Laurus camphora*) as dextro-camphor. This is the ordinary camphor of commerce, known as Japan camphor, whilst the less common laevo-camphor is found in the oil of *Matricaria parthenium*. Camphor can also be obtained by the oxidation of borneol or isoborneol with nitric acid. It forms a colourless, translucent mass, which crystallises well from alcohol ; it is easily sublimable at low temperatures. It melts at 175°, boils at 204°, and has a specific rotation of $\pm$ 44°. Inactive camphor, formed by the mixture of equal quantities of the oppositely active isomers, or by the oxidation of inactive borneol, melts at 179°. Camphor is the ketone of the alcohol borneol, and forms a number of well characterised crystalline derivatives. Amongst these are the semicarbazone, the phenylhydrazide, and the oxime, all characteristic of bodies containing the

.CO. group. The semicarbazone, $C_{10}H_{16}:N_2H.CO.NH_2$, melts at 236° to 238°. The hydrazide, $C_{10}H_{16}:N_2HC_6H_5$, results from the action of phenylhydrazine. The oxime, $C_{10}H_{16}.NOH$, is prepared by the action of hydroxylamine on camphor. It melts at 118°, and when reduced by means of sodium, yields the base bornylamine $C_{10}H_{17}NH_2$.

When distilled with phosphorus pentoxide, camphor yields cymene, and with iodine, carvacrol. Both of these bodies are *para*-derivatives of benzene. On oxidation with nitric acid, camphor yields many acids, of which the chief are camphoric acid $C_{10}H_{16}O_4$, camphanic acid $C_{10}H_{14}O_4$, and camphoronic acid $C_9H_{14}O_6$. The constitution of these acids has an important bearing on that of camphor. Many formulæ have been suggested for camphor during the past five years, but that of Bredt appears to have most evidence to support it. He considers that camphor consists of two five-carbon rings, connected in the following way:—



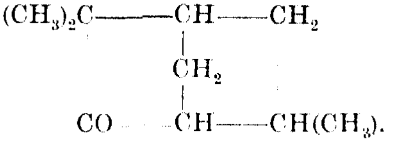
At all events it is practically certain that the expression $C_8H_{14}\langle\begin{smallmatrix}CH_2\\|\\CO\end{smallmatrix}$ correctly represents camphor, whatever its actual constitution may be. For full details of some of the most modern work on this intricate subject the reader should consult the following papers: (Bredt, *Ann. Chem.*, cclxxxix., p. 1; *Berichte*, 1896, *Ref.*, xx., p. 678); (Tiemann, *Berichte*, 1895, p. 1079; 1896, p. 122); (Baeyer, *Berichte*, 1895, p. 1599); (Béhal, *Comptes rendus*, cxix., pp. 799 and 858).

Fenchyl Alcohol, $C_{10}H_{17}OH$.—This alcohol is isomeric with, and closely analogous to, borneol. It was originally prepared by Wallach by reducing the ketone fenchone, a

natural constituent of several essential oils, by means of sodium. Later (*Annalen*, 1895, p. 324), he obtained it in fairly large quantities as a by-product in the preparation of fenchone-carboxylic acid, by passing a current of CO_2 through an ethereal solution of fenchone in the presence of sodium. Fenchyl alcohol, when quite pure, melts at 45° (not at 40°, as frequently stated). It boils at about 200°, and has a specific gravity of ·933 at 50°. It is known in both optically active varieties, that prepared from dextro-fenchone being laevo-rotary, whilst laevo-fenchone yields dextro-fenchyl alcohol. The specific rotation is ± 10·6°. Inactive fenchyl alcohol melts at 35°, and results from mixing the two isomers. Dehydrating agents, such as potassium bisulphate, abstract water, with the formation of the terpene, fenchene. A liquid chloride is obtained by the action of phosphorus pentachloride, which boils at 85°, under a pressure of 16 mm., and has a specific gravity ·983.

Fenchone, $C_{10}H_{16}O$. — This ketone occurs as dextro-fenchone in oil of fennel, and as laevo-fenchone in oil of Thuja. It can be extracted in a pure state from either of these oils by treating the fraction boiling at 190° to 195° with nitric acid, and steam distilling the product. When purified, it forms an oil of camphoraceous odour, boiling at 193°, of specific gravity ·946 at 19°, and solidifying at low temperatures, after which it melts at + 5° to + 6°. Its optical rotation is ± 72°. It can also be prepared by oxidising fenchyl alcohol, the optical activity being opposite in sign to that of the alcohol from which it is produced. The inactive form results from mixing equal quantities of the optically active varieties. On reduction, as above stated, it yields fenchyl-alcohol, $C_{10}H_{17}OH$. It forms an oxime, $C_{10}H_{16}NOH$, melting when quickly heated, at 161°. Numerous other derivatives are known, which are in many cases quite analogous to the corresponding camphor com-

pounds. Wallach considers that the ketone contains a four-carbon and a five-carbon ring, but Tiemann considers that the constitution is best expressed by the formula :—



Thujyl Alcohol, $C_{10}H_{17}OH$.—This body does not, apparently, occur in nature. It results from the reduction of its ketone, thujone, by means of sodium. It is identical with the body originally described by Semmler under the name tanacetyl alcohol. When pure it is a liquid boiling at 92° under a pressure of 13 mm., of specific gravity ·927. It yields a chloride, thujyl chloride $C_{10}H_{17}Cl$, by the action of phosphorus pentachloride, which on treatment with aniline yields up HCl, with the formation of the terpene thujene.

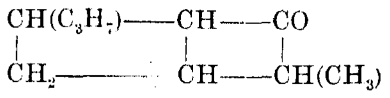
Thujone, $C_{10}H_{16}O$.—This ketone, isomeric with those above described, is found in the oils of thuja, tansy, wormwood and sage. It is identical with the bodies formerly described under the names tanacetone and salvone. It is best prepared in a state of purity from oil of wormwood. According to Semmler, 200 c.c. of the oil, 200 c.c. of a saturated solution of sodium bisulphite, 75 c.c. of water, and 300 c.c. of alcohol are well shaken at intervals during a fortnight. The crystals formed, consisting of the compound of thujone with the sodium bisulphite, are separated, washed with alcohol-ether and pressed. On treatment with caustic soda solution, the thujone, amounting to over 40 per cent. of the oil used, separates, and can be distilled with steam. Thujone is an optically active liquid $[a]_d = 68°$, boiling at 200° to 203°, of specific gravity ·917. By reduction with sodium it yields thujyl alcohol. It yields a number of characteristic crystalline derivatives, the most important being the oxime $C_{10}H_{16}.NOH$ melting at 55° and the semicarbazone $C_{10}H_{16}:N_2H.CO.NH_2$

melting at 171°. The various compounds of this ketone are closely analogous to those of the isomers already described.

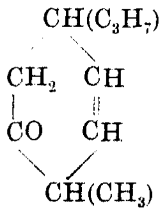
Thujone is easily converted into two isomeric ketones, isothujone and carvotanacetone. The former results by heating thujone with 40 per cent. sulphuric acid, whilst the latter is formed by heating thujone in a closed tube to 280°. The more interesting of these isomers is isothujone, for on reduction with sodium and alcohol, an alcohol $C_{10}H_{19}OH$ results, which is isomeric with menthol, and which is sufficiently similar to this body in its properties to be termed thujamenthol. Thujamenthol on oxidation yields the ketone thujamenthone, which is isomeric with ordinary menthone. Carvotanacetone yields corresponding compounds carvomenthol and carvomenthone. The physical properties of the isomers, thujone, isothujone and carvotanacetone are given by Wallach as follows:—

	Boiling Point.	*Specific Gravity.*	*Refractive Index.*
Thujone . .	200°-203°	·9175	1·45109
Isothujone . .	231°-232°	·9285	1·48217
Carvotanacetone	228°	·9373	1·48350

Tiemann gives the boiling point of thujone (tanacetone) as 203° and of carvotanacetone as 230°. The following are the formulæ which best express the relations of thujone and isothujone:—



Thujone.



Isothujone.

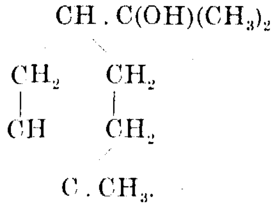
(In both these formulæ C_3H_7 represents the *iso*-propyl group.)

Terpineol, $C_{10}H_{17}OH$.—This alcohol, which now plays an

important part in the preparation of artificial perfumes, has long been a puzzle to chemists. Wallach prepared it by acting on terpin hydrate with dilute phosphoric acid. He stated that it was a monatomic alcohol, boiling at 215° to 218°, and described it as a liquid. Bouchardat and Tardy prepared it by the action of very dilute sulphuric acid on terpin hydrate, and found that it solidified on cooling and then melted at 30° to 32°, easily remaining in a state of superfusion. A closer examination by Wallach and Baeyer showed that the true melting point is 35°. A study of the two bodies, the "liquid" and the "solid" terpineol, and of their oxidation products (*Berichte*, 1895, p. 1781), indicates that either they are merely geometrical isomers, or that the liquid terpineol contains traces of impurity which prevent it from solidifying. At all events, it is these bodies which are sold as terpineol, and the solid compound is worth about four to five times as much as the liquid. They possess an odour recalling hyacinths, hawthorn and lilac, and are largely used for the preparation of these perfumes. Both are optically inactive, but Semmler has recently prepared optically active terpineols, by replacing the chlorine in the two limonene monohydrochlorides by the hydroxyl group. The resulting terpineol is optically active in the same direction as the limonene from which it is produced. Baeyer has, in addition, synthesised an *isomeric* terpineol, melting at 69° to 70°.

Terpineol (both the liquid and solid inactive, and the optically active varieties) possesses a strong odour of lilac and hyacinths. All of these varieties boil at from 215° to 218°, and have a specific gravity about ·945°. The inactive solid and liquid forms yield a phenylurethane, $C_{10}H_{17}O.CO.NH.C_6H_5$, melting at 113°. A close study of the oxidation products renders it almost certain that liquid terpineol is identical with the solid form, except for traces of some impurity, and that Semmler's active terpineols are

the optically active isomers of this body, all possessing the constitution—



Terpineol occurs in the free state in the oil of *Erigeron canadense*, and as the acetate in cajuput and cardamom oils.

Pulegol, $C_{10}H_{17}OH$, is the alcohol corresponding to the ketone, pulegone, from which it can be obtained by reduction with sodium. It is a viscous liquid, having the odour of terpineol, boiling at 215°, of specific gravity ·912. Isopulegol is the corresponding alcohol of isopulegone. This body boils at 91°, under a pressure of 12 mm., and has a specific gravity ·9154 at 17·5°. The ketones themselves are, however, of chief interest.

Pulegone, $C_{10}H_{16}O$, occurs in the oils of *Mentha pulegium* and *Hedeoma pulegoides*. It is a liquid ketone, combining with sodium bisulphite to form a crystalline compound, which, when decomposed, yields the ketone in a pure state. It then boils at 221°, and has a specific gravity ·936. It yields numerous characteristic derivatives, of which the oxime $C_{10}H_{16}NOH$ melts at 118°, and the semicarbazone at 172°. When hydrolysed by means of formic acid pulegone yields acetone and methyl-cyclohexenone $C_7H_{12}O$. When this body is again condensed with acetone, it yields a body isomeric with, and very similar to, natural pulegone. This body may be termed pseudo-pulegone. A second isomer, isopulegone, was obtained by Tiemann and Schmidt, by oxidising isopulegol, a body which they obtained in the form of its acetate by heating citronellal (*q. v.*) with acetic anhydride. Isopulegone boils at 85°, under a pressure of 13 mm. The pulegone and

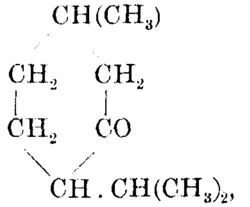
the isopulegone series of compounds are very similar in their physical and chemical properties, but they differ sharply in the fact that natural pulegol and pulegone yield some menthol when reduced with sodium, whilst isopulegol and isopulegone resist the action of the metal. The properties of the isomers are compared in the following table :—

	Boiling point.	*Specific gravity.*	*Rotation.*
Pulegol	103° at 15 mm. 215° at 760 mm.	·912 at 20°	—
Isopulegol	91° at 12 mm.	·916 at 18°	− 2·7°.
Pulegone	99° at 12 mm. 221° at 760 mm.	·936	+ 22·9°.
Isopulegone	85° to 90° at 13 mm.	·921 at 18°	+ 10·25°.
Pseudo-pulegone	94° at 14 mm. 215° at 760 mm.	·918 at 20°	—

Menthol, $C_{10}H_{18}OH$.—This important compound is a crystalline alcohol, which occurs to a very large extent in oil of peppermint, from which it may be separated by freezing. It can also be prepared experimentally, from its ketone, menthone, and, with other bodies, from pulegone, by reduction. Menthol forms fine white crystals, melting at 42°, boiling at 212°, and having a specific gravity ·890 at 15°. When obtained from oil of peppermint it is laevorotary, about − 59°. Careful oxidation converts it into menthone, the corresponding ketone. Menthol has all the ordinary properties of an alcohol, and forms well-defined esters with the organic acids. Of these menthyl acetate, $C_{10}H_{19}O.CO.CH_3$, is of the most frequent occurrence in nature. It is a liquid of penetrating odour, boiling at 224°. The relations of menthol to menthone are the same as those of borneol to camphor, and there is a close similarity between many of their derivatives.

Menthone, $C_{10}H_{18}O$, occurs with menthol in oil of peppermint. According to the early work of Moriya, this body was described as optically inactive, but this has been shown to be incorrect. Atkinson describes it as an oily liquid, boiling

at 206°, with a rotary power of 21°. Beckman gives 208° as its boiling point, and 26° to 28° as its optical activity. Its specific gravity is ·894. Oxidation of natural menthol produces laevo-menthone, but this is easily converted into dextro-menthone by the action of acids. This, on reduction, yields dextro-menthol. The various derivatives of the optically active isomers correspond closely, but complicated stereo-chemical relationships exist, which render the chemistry of their derivatives a very difficult question. The oximes of the two isomers do not correspond in their properties, that of dextro-menthone being a laevo-rotary oil, whilst that of laevo-menthone is a solid, melting at 59°. The semicarbazone melts at 184° in both cases. There are numerous bodies isomeric with, and closely similar to, those of the menthone series. Those of the thujamenthol and carvomenthol series have already been mentioned. Menthone, in all probability, has the constitution—



menthol being, of course, the corresponding alcohol.

Cineol, $C_{10}H_{18}O$.—This body, which is somewhat isolated in its chemical relationships, may well be discussed here. It has been described under several names, the best known being that now usually adopted, *viz.*, cineol; also cajuputol (from its occurrence in oil of cajuput), and eucalyptol (from its occurrence in oil of eucalyptus). It is found in nature in very large quantities in the above-mentioned oils, as well as in many others, notably wormseed, lavender (English), and spike-lavender oils. It results also by the treatment of terpin hydrate with acids. Wallach and Brass, who first

characterised it as a definite compound, gave the following method for its preparation. A current of dry hydrochloric acid gas is passed into rectified wormseed oil. The resulting crystalline magma of cineol hydrochloride is pressed at low temperature to remove as much as possible of adhering liquid, and the crystals are treated with water and steam distilled. The crude cineol is again subjected to this treatment, when the pure body is obtained. When pure, cineol is an optically inactive liquid, solidifying at low temperatures and melting at -1°, with a characteristic camphoraceous odour. It boils at 176°, and has a specific gravity ·930. Its refractive index is 1·4559. Scammell proposed its separation by means of a definite crystalline compound with phosphoric acid. This body has the composition $C_{10}H_{18}O.H_3PO_4$. The use of phosphoric acid is the basis of the 1898 British Pharmacopœial test for cineol in essential oils.

Cineol forms a number of crystalline derivatives, amongst which may be mentioned the hydrobromide, $C_{10}H_{18}O.HBr.$, melting at 56°, and the compound with iodol, $C_{10}H_{18}O.C_4I_4NH$, which forms yellowish-green crystals, melting at 112°. These are both useful for identifying cineol. According to all reliable observations, the oxygen atom in cineol does not possess alcoholic, ketonic, aldehydic or acid functions. Apparently it is quite indifferent, which accounts for the isolated nature, chemically speaking, of the compound. Its relationships are certainly chiefly with the terpenes. In commerce, this body finds considerable employment under its other name, eucalyptol.

III. The Geraniol and Citronellol Group.

This group of bodies has attracted a great deal of attention from a number of well-known chemists during the past five or six years, and although we now understand something of the chemical relationships of the various members of the

group, much is still a matter of conjecture and uncertainty. The more important compounds in this category are of the same empirical composition as the members of the camphor group, but are entirely different from them in their actual constitution. They belong, indeed, to the aliphatic or open chain series of compounds.

It will be convenient to study this group under the two headings—geraniol and citronellol, these being the most important of its members. From time to time, various observers have announced the discovery and separation of aromatic alcohols (*i.e.*, *sweet smelling*, not belonging to the *aromatic* series) in certain essential oils, notably those of rose, geranium, neroli, citronella, linaloe, bergamot, lavender, limes, basil, petit-grain, coriander, and cananga, of the formula $C_{10}H_{18}O$. In general the properties of these alcohols were very similar, although not, in many cases, identical. Exhaustive and very thorough investigations, chiefly by Tiemann and Semmler have gone far to prove that they are in nearly every case more or less impure forms of two chemical individuals. These are geraniol and linalol, which we shall discuss immediately.

A short summary of some of the other alcohols whose claims to chemical individuality are now practically abandoned will, however, be useful. Aurantiol was announced by Semmler and Tiemann to exist as an acetate in oil of petit-grain. Its specific gravity was given by them as ·869 at 20°; it combines with four atoms of bromine; is laevo-rotary; refractive index 1·4682. Later on the same chemists agreed that this body was slightly impure linalol.

Coriandrol, announced by Barbier, was found in oil of coriander. Its properties were given as follows: boiling point, 196° to 198°; specific gravity at 0°, ·882; refractive index, 1·464; rotary power, + 15° 1′. Barbier considered that this was dextro-rotary licareol. The latter was found

in the oil of *licari kanali*, and its properties were almost exactly identical with those of coriandrol, except that its optical activity was of the opposite sign. By the action of acetic anhydride, an acetate is formed, which Barbier claimed yielded a fresh alcohol, licarhodol, on saponification. This, he urged, was a stable isomeride of licareol. Bertram, however, in 1894, stated that licarhodol was merely geraniol, but Stephan has recently (*Jour. prakt. Chem.*, 1898, p. 111) shown that it also contains active terpineol. Bourchardat also claimed that licareol was identical with linalol.

Nerolol, obtained from oil of neroli, was speedily recognised by Tiemann as identical with linalol.

Rhodinol was announced by Eckart to be an essential ingredient of Turkish and German rose oils. He regarded it as an unsaturated open chain alcohol. Markovnikoff thereupon urged that roseol, $C_{10}H_{20}O$, was the chief ingredient of rose oil, and much controversy has gone on between a number of continental chemists, as to the real identity of the body. Bertram, in 1894, claimed that it was in reality merely geraniol, but in 1896 Tiemann and Schmidt showed that the alcohols of rose oil consisted of a mixture of geraniol and citronellol, $C_{10}H_{20}O$, which latter body had evidently been mistaken for the so-called "rhodinol" and "roseol".

The names geraniol and citronellol therefore appear to be those most entitled to remain in chemical literature. Poleck, however, complains that the name geraniol has been substituted for the earlier rhodinol, overlooking the fact that the old rhodinol is clearly a mixture. Erdmann further complicates this matter by insisting on treating geraniol of commerce as a more or less impure body of which the principal constituent, $C_{10}H_{17}OH$, is called rhodinol, claiming that geraniol (pure) and rhodinol are identical, and that the former should be expunged from chemical literature. But the mass of evidence is in favour of the retention of the

name geraniol, and it is to be hoped that the polemics now obtaining in regard to this question will soon cease.

The last of these doubtful bodies to be mentioned is reuniol, found in various geranium oils (Réunion, African, and Spanish) by A. Hesse. This had previously been announced as a probable chemical individual by Barbier, but he stated that he had not obtained it pure. Erdmann and Huth claim that it is more or less pure rhodinol, that is, geraniol.

Geraniol, $C_{10}H_{18}O$, is thus the most important alcoholic constituent of this group of essential oils. It is a colourless oily liquid, of pleasant rose-geranium odour, but lacking the fine character of the oils in which it occurs. It possesses the following properties. It boils at 229° to 230° under ordinary pressure, and at 120° under a pressure of 16 mm. Its specific gravity is about ·881, and its refractive index 1·4776. It is optically inactive. By means of its refractive index (Brühl's theory), and its ready combination with four atoms of bromine, it is shown to contain two ethylene unions, hence it cannot be a closed chain compound. By careful oxidation with chromic acid it yields its aldehyde, citral, and by heating in an autoclave with water to 200° it is partly converted into its isomer, inactive linalol. It yields an acetate when acted upon by acetic anhydride, which also occurs in nature. This is a fragrant oil, of specific gravity ·9174, boiling at 128° to 129°, under a pressure of 16 mm., which occurs naturally in several essential oils.

To purify geraniol and separate it in a state of absolute purity, Tiemann and Kruger recommend dissolving sodium in the alcohol, treating the sodium alcoholate with ether and phthalic anhydride; the resulting geraniol sodium phthalate is hydrolysed by alcoholic potash, and the pure geraniol precipitated by the addition of water.

To detect geraniol in essential oils, Jacobsen recommends

the following process, provided that the amount present exceeds 25 per cent. The dry oil is intimately mixed with an equal weight of dry powdered calcium chloride, and the mixture kept in a desiccator at -4° for twelve to sixteen hours. The soft mass is rubbed up with dry benzene, ether, or petroleum ether, and the liquid portion removed by a suction filter. The calcium chloride compound of geraniol is then treated with water, and the oil separated, washed and distilled, when geraniol passes over at 228° to 230°. Another useful method for its identification, which was discovered by Erdmann, consists in heating the alcohol with diphenyl-carbamine chloride and pyridine in a water bath. Unaltered products and diphenylamine are removed by steam distillation, and the residue crystallised from alcohol. The pure geraniol diphenylurethane resulting, crystallises in colourless needles, melting at 83°. An ethereal pseudo-salt, which forms crystals melting at 49°, has recently been described by Erdmann. It is obtained by heating the alcohol with opianic acid, when the two bodies combine to form the crystalline compound. According to Tiemann and Semmler, who have worked for many years on geraniol, its constitution is—

$$(CH_3)_2C : CH . CH_2 . CH_2 . C(CH_3) : CH . CH_2OH.$$

Linalol, $C_{10}H_{18}O$, is isomeric with geraniol, but, as it is known in both the optically active forms, as well as in the inactive, it is certainly not a stereoisomer of this body. It was first discovered in oil of linaloe, of which oil it is the most important constituent. It is a pleasant-smelling liquid, and occurs both free and combined as the acetate, in various oils, notably those of linaloe, lavender and bergamot. It is an oily liquid, boiling at normal pressure at about 198°, and at 86° to 87° at 14 mm. Its specific gravity is ·872 at 15·5°, and refractive index, 1·4611. These figures are from a specimen obtained from licari oil. A sample from linaloe oil gave a higher specific gravity, *viz.*, ·8765 at 17·5°. The

optical activity is not known with certainty. Probably it is about ± 20°. On oxidation it yields, amongst other products, geranaldehyde. Bouchardat states that if linalol is treated with acetic anhydride at low temperatures, an acetate is formed, which regenerates linalol on hydrolysis, but that at elevated temperatures a new alcohol is formed. This, however, has since been shown to be a mixture of geraniol and terpineol. Linalyl acetate, $C_{10}H_{17}O . COCH_3$, is the important constituent of bergamot oil, and occurs in many other oils also. It is an odoriferous liquid of specific gravity ·912, boiling at 105° to 108° at 11 mm. It can be prepared by the action of acetate anhydride on linalol. Its close connection with geraniol, together with a study of its derivatives, cause Tiemann and Semmler to assign to linalol the formula:—

$$CH_3 . C(CH_3) : CH . CH_2 . CH_2 . C(CH_3)(OH) . CH : CH_2.$$

Geranaldehyde, $C_{10}H_{16}O$. — This body, which is the aldehyde of geraniol, and is known generally by the name citral, occurs to a considerable extent in many oils of the *Citrus* family. It is highly odoriferous, and is, to a great extent, responsible for the perfume of several oils. Lemon oil, orange oil, the oil of *Eucalyptus maculata* (var., *citriodora*) and lemon-grass oil all contain citral, the two last named in considerable proportion. It can also be obtained by the oxidation of its alcohol, geraniol, by means of chromic acid. To prepare it from this source, 10 grammes of potassium bichromate are dissolved in a mixture of 12·5 grammes of sulphuric acid and 100 grammes of water; 15 grammes of geraniol are then added. The mixture should be kept well cooled at first, and allowed to become warm afterwards, and well shaken for half an hour. It is then rendered slightly alkaline, and distilled in a current of steam. To separate the aldehyde from other products, the distillate is mixed with a saturated solution of sodium bisulphite, and

allowed to stand for twenty-four hours, with occasional shaking. It forms a crystalline compound with the bisulphite, which is separated, pressed between blotting paper, washed with ether, and mixed with sodium carbonate, and steam distilled. Citral can also be obtained from essential oils, such as lemon-grass oil, by means of the bisulphite process, but care should be taken that the temperature be kept low, as otherwise a considerable loss occurs, due to the conversion of part of the citral into sulphonic acid compounds. Pure citral boils at about 228° to 230° under ordinary pressure, and at 110° under a pressure of 12 mm. It is an oily liquid of specific gravity ·8972, and refractive index 1·4931, but optically inactive. It combines with 4 atoms of bromine, and, under the influence of dehydrating agents, such as potassium hydrogen sulphate, yields cymene, $C_{10}H_{14}$. Under the influence of alkalies, citral condenses with acetone, with the splitting off of water to form pseudo-ionone, $C_{13}H_{20}O$, which is converted into its isomer ionone by means of acids. This body is the characteristic artificial violet perfume, which will be mentioned later. Reduction with sodium and alcohol produces the alcohol, geraniol. Various derivatives of citral have been prepared, such as the oxime, anilide and phenylhydrazone, which are oily liquids, and the semicarbazone, which appears to exist in several isomeric forms of different melting points. Most characteristic, however, is the citryl-β-naphtocinchonic acid, discovered by Doebner. This can be prepared by warming together in alcoholic solution 20 parts of citral, 20 parts of β-naphtylamine and 12 parts of pyruvic acid. This acid, $C_{23}H_{23}NO_2$, melts sharply at 197°, and is the most useful compound for characterising citral. Indeed, Doebner has applied its preparation to the quantitative estimation of citral in oils containing it. The determination of this body in essential oils is by no means an easy matter, and will be mentioned

later. A study of citral and its derivatives has caused Tiemann to assign to it the formula based on that of geraniol, *viz.*:—

$$(CH_3)_2 . C : CH . CH_2 . CH_2 . C(CH_3) : CH . CHO.$$

During the past twelve months Tiemann has carried out a great deal of work on the chemistry of citral (*Berichte*, xxxi., pp. 3278, 3324; xxxii., p. 107), in connection with which the following points are especially noteworthy. He has shown that in addition to the normal bisulphite of sodium compound of citral, three hydrosulphonic acid derivatives are formed, according to the conditions under which the experiment is performed (acidity, alkalinity, temperature, etc.). He attempts to explain the existence of two well-defined isomeric semicarbazones (melting at 164° and 171°) by suggesting that two stereoisomeric forms of citral are present in lemon-grass oil. To support this, he mixes the normal bisulphite compound with water and adds sodium carbonate. The liquid is then shaken with ether, and about half the citral is set free and dissolves in the ether (fraction *a*); the remainder is set free by the addition of caustic alkali and extracted with ether (fraction *b*). Whilst both fractions have exactly the same physical properties, it is found that fraction *a* gives only one semicarbazone, melting at 164°, whilst fraction *b* gives both, melting at 164° and 171° respectively. The same was found to be the case with the cyanacetic compound, fraction *a* yielding only one citralidene cyanacetic acid melting at 122°, whilst fraction *b* gave this, and also one melting at 80°.

Professor Tiemann has also shown that by condensation of citral with cyanacetic acid, a citralidene cyanacetic acid

$$C_9H_{15} . CH : C\begin{cases} CN \\ COOH \end{cases}$$

is formed which crystallises in fine crystals, and melts at

122°. This compound is very well adapted for the detection and for the approximate quantitative determination of citral in essential oils. The behaviour of citral towards semicarbazide has also been used for the detection of the aldehyde, without, however, giving a satisfactory result, because mixtures of semicarbazones with different melting points (130° to 170°) are formed.

For the quantitative determination of citral in lemon-grass oil the use of indirect methods is preferable. The aldehyde is converted into the normal, slightly soluble sodium bisulphite compound, by agitating the oil with sodium bisulphite solution containing acetic acid, or, by the action of an alkaline solution of sodium cyanacetate, into the readily soluble sodium citralidene cyanacetate, or also, by the action of sodium sulphite and sodium bicarbonate, into sodium citraldihydrodisulphonate. The non-aldehydic compounds are separated from the citral-derivatives formed by agitation with ether, and are weighed after the evaporation of the solvent. The difference between the weight of the oil used for the determination, and the weight of the non-aldehydes represents approximately the amount of citral.

Citronellol, $C_{10}H_{20}O$, is an alcohol closely related to geraniol. It was first obtained by Dodge, by reducing the aldehyde citronellal, $C_{10}H_{18}O$, by means of sodium amalgam and acetic acid. Later Tiemann and Schmidt showed that the alcoholic constituents of oil of roses consisted of geraniol and citronellol. Spanish geranium oil also contains citronellol, in both the *dextro-* and the *laevo-*rotary forms. It is an odoriferous oil, boiling at 117° to 118° under a pressure of 17 mm., has a specific gravity ·8565 at 17·5°, and a refractive index 1·4566; its specific rotary power is about 4°. Citronellol, obtained by reducing the aldehyde, is dextro-rotary; that from oil of roses is laevo-rotary, whilst in most geranium oils both varieties exist. It forms an

acetate, an oily liquid of characteristic odour, of specific gravity ·8928 at 17·5°, boiling at 120°, under a pressure of 15 mm., and with an optical activity $[a]_d = 2·4°$.

A number of characteristic derivatives have been prepared and described by Semmler. The oxime, $C_{10}H_{18}NOH$, boils at 135° to 136° under a pressure of 14 mm., and has a specific gravity ·9055 at 20°. Citronellic acid, $C_{10}H_{18}O_2$, obtained by the action of silver oxide and ammonia on the aldehyde, boils at 143° under a pressure of 10 mm., and at 257° at 760 mm. Its specific gravity is ·9308 at 20°. The stereoisomeric relationships of the two forms of citronellol are demonstrated by the fact that they both yield β-methyl-adipic acid when oxidised; this, however, is *dextro-* or *laevo-*rotary, according to the activity of the citronellol from which it is produced.

Although belonging to the closed-chain series of compounds, several members of the menthone group are very closely related to the bodies just described. Tiemann obtained a closed-chain alcohol, isopulegol, $C_{10}H_{18}O$, by heating citronellal with acetic anhydride in an autoclave. This, on oxidation with chromic acid, yields isopulegone, $C_{10}H_{16}O$, the corresponding closed-chain ketone, isomeric with natural pulegone (the characteristic constituent of oil of pennyroyal), which is probably of the constitution—

$$(CH_3)HC\begin{matrix} CH_2 - CO \\ CH_2 - CH_2 \end{matrix}C : C(CH_3)_2.$$

By acting on isopulegone with barium hydroxide, it is completely converted into ordinary pulegone.

Wallach has recently succeeded in reversing the change, and has prepared from menthone (the ketone corresponding to menthol, and a body closely allied with pulegone) an open-chain compound which he calls mentho-citronellol. Menthone, $C_{10}H_{18}O$, is converted into its oxime, $C_{10}H_{18}.N.OH$,

which when heated with phosphoric anhydride yields the corresponding nitrile $C_9H_{17}.CN$. On reduction this gives menthonylamine $C_9H_{17}.CH_2.NH_2$, and this, by the action of nitrous acid, gives mentho-citronellol, according to the equation—

$$\underset{\textit{Menthonylamine.}}{C_9H_{17}.CH_2.NH_2} + NO.OH = \underset{\textit{Mentho-citronellol.}}{C_9H_{17}.CH_2OH} + N_2 + H_2O.$$

Wallach assigns to this body the same constitution as that attributed to citronellol by Tiemann and Schmidt, *viz.*, $C(CH_3)_2 : CH . CH_2 . CH_2 . CH (CH_3) . CH_2 . CH_2 . OH$. On oxidation this body yields mentho-citronellal $C_9H_{17}.COH$, but this is not identical with ordinary citronellal. The relations between the ordinary citronellol series and these new bodies require further explanation.

The frequent occurrence of citronellal and citral, and of citronellol and geraniol, together in essential oils makes it a matter of some importance to be able to effect a separation of the bodies. For the former case Doebner gives the following method. The oil is digested with pyruvic acid and β-naphthylamine, when condensation products of the aldehydes with β-naphtho-cinchoninic acid are formed. The citral compound is less soluble than the other and therefore crystallises out. The citronellal compound melts at 225°, whilst that of mentho-citronellal melts at 214°, which proves that they are not identical.

Flatau and Labbé have published a method for the separation of citral from citronellal which depends upon the fact that the aqueous solution of the sodium bisulphite compound of citral gives no precipitate with barium salts, while the insoluble barium bisulphite of citronellal is quantitatively precipitated. The separation of a mixture of both aldehydes is effected in the following way. Firstly, the normal sodium bisulphite compound of the aldehydes is prepared and dissolved in water; this is precipitated by barium chloride

and the precipitate of the citronellal compound is collected upon a filter. From the filtrate, the citral is isolated by the addition of alkali, and by shaking the fluid with ether. The barium sulphite compound of citronellal is agitated with alcoholic potash, avoiding heating, and is separated by filtration from the barium and potassium sulphites formed. In order to remove the excess of alkali, the filtrate is saturated with carbonic acid gas, once more filtered, and the citronellal, separated from the solution by the addition of water, taken up by ether. By means of this method, Labbé has succeeded in obtaining besides 70 per cent. of citral, 6 per cent. of citronellal from oil of lemon-grass. In the same way citronella oil was found to contain 25 to 30 per cent. of citronellal, and 2 to 5 per cent. of citral.

To separate citronellol and geraniol Tiemann and Schmidt heat the liquid with an equal weight of phthalic anhydride to 200° for about two hours. Geraniol is thus converted into a hydrocarbon, whilst citronellol is converted into a phthalic acid compound, which is shaken out with dilute potash and washed free from hydrocarbons with ether, and hydrolysed. The citronellol is thus set free. The same chemists have succeeded in separating citronellol when occurring in very small proportion in geraniol, by a method depending on the conversion of the citronellol into its phosphate and then separating this. Briefly, the method consists in acting on the mixture of geraniol and citronellol with phosphorus trichloride, using ether as the solvent. 100 parts of the alcohols in 100 parts of absolute ether are cooled to − 10° and gradually added to 60 parts of phosphorus trichloride in 100 parts of ether, also cooled to − 10°. The temperature must not rise above 0° till the mixture is complete. It is then allowed to stand for four to five days at the ordinary temperature. The ethereal solution is then mixed with powdered ice and washed with ice water. After a second

washing with ice-water, it is washed with solution of soda, which extracts a citronellyl-phosphoric acid, leaving geranyl chloride in the ether. The aqueous solution of the sodium salt of the citronellyl-phosphoric acid is washed with ether, and then saponified with strong alkali, and the citronellol distilled over with steam.

The probable constitution of citronellol is :—

$C(CH_3)_2 : CH . CH_2 . CH_2 . CH (CH_3) . CH_2 . CH_2 OH.$

Citronellal, $C_{10}H_{18}O$, is the aldehyde of citronellol, and occurs in several essential oils, notably in citronella oil, in which it was first discovered by Dodge, who separated it by means of its bisulphite compound. It is an oily liquid of characteristic odour, of specific gravity ·8768 at 17·5°, and refractive index 1·4481. It is dextro-rotary, $[a]_d = + 8·18°$. On reduction it yields the alcohol, citronellol, $C_{10}H_{20}O$. It boils at 205° to 208° under ordinary pressure. It forms numerous characteristic derivatives, of which the oxime $C_{10}H_{18} . NOH$ is an oil boiling at 135° at 14 mm., of specific gravity ·906. It also forms a compound with phosphoric acid, which combines with aniline, the resulting salt melting at 165°. It appears almost certain that citronellol and citronellal are dihydro-derivatives of geraniol and geranial (citral). Citronellal has in all probability the constitution—

$C(CH_3)_2 : CH . CH_2 . CH_2 . CH (CH_3)CH_2 . COH.$

Methyl-heptenone, $C_8H_{14}O$.—This body is an open-chain ketone of the constitution $CH_3 . C(CH_3):CH.CH_2.CH_2.CO.CH_3$, according to Tiemann. It occurs naturally in oil of lemongrass and other oils, and results from the oxidation of citral, or the distillation of cineolic anhydride. Many discordant statements have been made as to the identity or otherwise of this ketone when extracted from different oils, but Tiemann's recent work tends to prove that natural methyl-heptenone has the formula given it above and is identical with that obtained from cineolic anhydride. It is best identified by its semicarbazone melting at 134°.

The Geraniol and Citronellol Series.

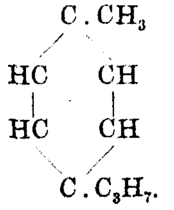
	Boiling Point.	Sp. Gravity.	Refractive Index.	Optical Activity.	B. P. of Acetate.	Sp. Gr. of Acetate.	Oxime.	Semicarbazone.
Geraniol $C_{10}H_{17}.OH$	229°-230°	·880-·883	1·4776	inactive	128°-129° at 16 mm.	·9174 at 15°	—	—
Linalol $C_{10}H_{17}.OH$.	195°-198°	·872	1·4611 at 20°	about ± 20°	105°-106° at 11 mm.	·912 at 15°	—	—
Citronellol (dextro) $C_{10}H_{19}.OH$ . .	117°-118° at 17 mm.	·856 at 17·5°	1·4566 at 20°	+ 4°	119°-121° at 15 mm.	·893 at 17·5°	—	—
Citronellol (laevo) $C_{10}H_{19}.OH$ . .	113°-114° at 15 mm.	·861 at 20°	1·4579 at 20°	- 4·3°	—	—	—	—
Citral (geranaldehyde) $C_{10}H_{16}O$.	228°-229°	·897 at 15°	1·4931 at 15°	inactive	—	—	$C_{10}H_{16}$: NOH, liquid b.p. 143° at 12 mm., sp. gr. at 20° = ·9386	$C_{10}H_{16}$: $N_2H.CONH_2$ m.p. = 135°
Citronellal (dextro) $C_{10}H_{18}O$ . .	205°-208°	·875 at 17·5°	1·4481 at 20°	+ 8·2°	—	—	$C_{10}H_{18}$: NOH, liquid b.p. 135° at 14 mm., sp. gr. at 20° = ·9055	$C_{10}H_{18}$: $N_2H.CONH_2$ m.p. = 82·5°
Citronellal (laevo) $C_{10}H_{18}O$ . .	143°-144° at 14 mm.	—	1·4536 at 20°	- 6·25°	—	—	—	—

IV. Benzene Compounds.

A large number of compounds, belonging to what is usually termed the *benzene series*, occur in essential oils. Comparatively few, however, are of common occurrence, and these are mainly either phenols or alcohols and their immediate derivatives, aldehydes or acids. Of bodies outside these limits, the hydrocarbon cymene is probably that of most frequent occurrence. The following paragraphs deal briefly with the most important of these bodies :—

Cymene.

Cymene, $C_{10}H_{14}$.—There are a number of isomeric bodies of this formula, which are either propyl-methyl-, or isopropyl-methyl-benzene. That which is usually known as cymene, however, and which occurs, for example, in Roman caraway oil, is the *para*-methylpropyl-benzene, that is, the isomer in which the methyl and the propyl groups are in the positions 1 and 4, according to the usually accepted notation for benzene derivatives. This body, then, has the constitution—



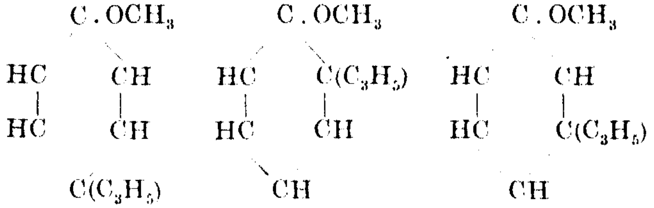
It is a pleasant-smelling liquid, boiling at 175° to 176° ; of specific gravity ·8722 at 0°. It can be obtained by distilling camphor and phosphorus pentoxide, or by boiling cumic alcohol with zinc dust ; or by heating *para*-bromtoluene with sodium and propyl iodide.

PHENOLS AND THEIR DERIVATIVES.

PHENOLS WITH NINE CARBON ATOMS.

Chavicol, $C_9H_{10}O$, is the only nine-carbon phenol of note which is found naturally in the free state in essential oils. It is *para*-allyl phenol, of the constitution, $C_6H_4(OH)(CH_2 . CH : CH_2)$. It occurs in the oil of *Chavica Betle*, and is a colourless oil of strong odour, of specific gravity 1·035 at 20°, boiling at 237°. It yields no colouration with ferric chloride. It yields a series of ethers, such as methyl- and ethyl-chavicol. The phenol *Anol* is very closely related to chavicol, being *para*-propenyl phenol, $C_6H_4(OH)(CH : CH . CH_3)$. It occurs naturally only in the form of ethers, the chief of these being *anethol*, $C_{10}H_{12}O$, which is its methyl ether, of the constitution $C_6H_4(O . CH_3)(C_3H_5)$. This body occurs in oil of aniseed, from which it can be separated in the form of white shining scales, melting at 21°, and boiling at 232°. It has been prepared synthetically from *p*-methoxyphenylcrotonic acid. It also results by means of a reaction common to this group of phenols. Methyl chavicol, above described, contains the allyl group, whilst anethol contains the propenyl group. It has been found that nearly all *allyl-benzene* derivatives are transformed into the isomeric *propenyl-benzene* derivatives, when heated with alcoholic potash. Methyl-chavicol in this way yields anethol. In this group of natural compounds the *propenyl* derivatives usually have higher specific gravities and boiling points than the corresponding *allyl* derivatives. Anethol is characterised by the formation of a brom-anethol dibromide, $C_6H_3Br.(OCH_3)(C_3H_5Br_2)$, melting at 107°. Compounds isomeric with anethol, in which the propenyl and the phenolic groups are in the *ortho-* and *meta*-positions, have been prepared by acting on the *ortho-* and *meta*-salicylic aldehydes with propionic anhydride and sodium propionate.

The relations of these to natural anethol are shown in the following diagrammatic formulæ :—



Natural Anethol. *Ortho-Anethol.* *Meta-Anethol.*

Allyl-dioxybenzene, $C_9H_{10}O_2$, is capable of existing in six possible isomeric forms. Of these only one is of any importance, and that only in the form of its ethers. *Eugenol*, *chavibetol* and *safrol* are all derivatives of the phenol :—

$$C_6H_3\begin{cases} C_3H_5 & (1) \\ OH & (3) \\ OH & (4), \end{cases}$$

when C_3H_5 is the allyl group, and the numbers refer to the position of the radicles in the benzene nucleus.

Eugenol, $C_{10}H_{12}O_2$, is its methyl ether of the constitution $C_6H_3(C_3H_5)^1(OCH_3)^3(OH)^4$. It occurs in the oils of cloves, allspice, bay and cinnamon leaves, and is a body of enormous commercial interest, on account of its use for the manufacture of vanillin (*q. v.*). It can be obtained in a state of comparative purity by shaking oil of cloves with alcoholic solution of potassium hydroxide. The whole solidifies to a crystalline mass. This is pressed, washed with alcohol and decomposed with an acid. The resulting oil, when washed to free it from traces of acid, can be purified by distillation. It is then a nearly colourless oil, of specific gravity 1·070, and boiling at 247°. It is coloured blue by ferric chloride. By oxidation with potassium permanganate, it is converted into vanillin and allied bodies. Various ethers of eugenol also exist, methyl-eugenol, $C_6H_3(OCH_3)_2(C_3H_5)$, being a constituent of several essential oils. It can also be formed synthetically

by the action of potash and methyl iodide on eugenol. Eugenol behaves in the manner above referred to when treated with hot alcoholic alkali, that is, it is converted into the corresponding propenyl compound, isoeugenol.

Chavibetol, $C_{10}H_{12}O_2$, is very closely related to eugenol, differing from it only in that the *hydroxy-* and the *methoxy-* groups are in the reversed positions. It is a methyl ether of allyl-dioxy-benzene, of the formula, $C_6H_3(C_3H_5)^1(OH)^3(OCH_3)^4$. It occurs with chavicol in oil of betel.

Safrol, $C_{10}H_{10}O_2$, is the methylene ether of allyl-dioxy-benzene, of the constitution—

$$C_6H_3\left\{\begin{array}{ll} C_3H_5 & (1) \\ O \diagdown & (3) \\ \quad\quad CH_2 & \\ O \diagup & (4). \end{array}\right.$$

It is found to a considerable extent in oils of sassafras, camphor and *Ilicium religiosum*. When pure it is a white crystalline mass at low temperatures, melting at + 8°. At ordinary temperatures it forms a colourless oil of characteristic, pleasant odour, of specific gravity about 1·1, and boiling at 232°. It is optically inactive when pure. It is easily converted into isosafrol (containing the propenyl group) by the action of alcoholic potash. Safrol is used to an enormous extent for perfuming cheap soaps, and is also of great commercial value on account of the fact that on oxidation it yields heliotropin, an artificial perfume which is now largely employed (*q.v.*).

Propenyl-dioxybenzene, $C_9H_{10}O_2$, is a phenol analogous in every respect to allyl-di-oxybenzene. The difference between the two bodies is that the latter contains the allyl group $.CH_2.CH:CH_2$, whilst the former contains the propenyl radicle $.CH:CH.CH_3$.

Isoeugenol, $C_{10}H_{12}O_2$, and *isosafrol*, $C_{10}H_{10}O_2$, are the two best known derivatives of this phenol. Isoeugenol results, according to the general rule of phenols containing

the allyl group, when eugenol is boiled with alcoholic potash. It is also obtained by distilling homoferulic acid with lime. It is an oil boiling at 260°. Its constitution is identical with that of eugenol, $C_6H_3(C_3H_5)^1(OCH_3)^3(OH)^4$, except that C_3H_5 here represents the propenyl group. Isosafrol, $C_{10}H_{10}O_2$, is obtained in the same manner from safrol, *viz.*, by boiling it with alcoholic potash. It is an oil, boiling at 248°, and solidifying at very low temperatures. Oxidation yields chiefly piperonal (artificial heliotropin).

Propenyl-trioxybenzene, $C_9H_{10}O_3$, is represented by its trimethyl ether, of the constitution $C_6H_2(C_3H_5)(OCH_3)_3$, which is *asarol*. This forms the solid constituent of the oil of *Asarum Europaeum* and occurs in monoclinic prisms, melting at 61° and boiling at 295° to 296°. Its specific gravity at 18° is 1·165. This constitution has quite recently received definite confirmation by the synthesis of the body by Gattermann, who condensed oxyhydrokinone-trimethyl ether and hydrocyanic acid in benzene solution, by means of aluminum chloride, and treated the reaction product with water. Asaraldehyde resulted, of the formula $C_6H_2\begin{cases}(OCH_3)_3\\ COH\end{cases}$, which was condensed with propionic anhydride and sodium propionate. Asarol, $C_6H_2\begin{cases}(OCH_3)_3\\ CH:CH.CH_3\end{cases}$, identical with the natural body resulted (*Berichte*, 1899, p. 290).

Allyl tetroxybenzene, $C_6H(C_3H_5)(OH)_4$, is represented by its dimethyl-methylene ether, *apiol*, $C_{12}H_{14}O_4$. Two isomers of this constitution, differing only in the relative positions of the substituent groups in the benzene nucleus, are well known, *viz.*, apiol from oil of parsley, and dill-apiol from some varieties of dill oil. The corresponding propenyl compounds, in which the allyl group is replaced by the propenyl radicle are also known. Apiol from oil of parsley

4

is a crystalline solid, volatile with steam, melting at 30° and boiling at 294°. It dissolves in strong sulphuric acid with a characteristic blood-red colour. By boiling it with alcoholic potash the allyl group suffers rearrangement, and isoapiol, the isomeric methylene-dimethyl ether of propenyl-tetroxy-benzene, results. This is also a crystalline solid, forming leaflets melting at 56° and boiling at 304°. In 1896 Ciamician and Silber announced the discovery of an isomeric apiol, which they separated from the high boiling fractions of oil of dill. It is an oily liquid, boiling at 285° with slight decomposition. When boiled with alcoholic potash it yields the so-called iso-dill-apiol, which differs from it in containing the propenyl instead of the allyl group. This body melts at 44° and boils at 296° with slight decomposition. A close study of these bodies has made it clear that the two isomeric apiols possess the formulæ—

$$C_6H\begin{cases}O_2CH_2 & (5 \text{ and } 4)\\ OCH_3 & (3)\\ OCH_3 & (2)\\ C_3H_5 & (1)\end{cases} \qquad C_6H\begin{cases}OCH_3 & (5)\\ O_2CH_2 & (4 \text{ and } 3)\\ OCH_3 & (2)\\ C_3H_5 & (1),\end{cases}$$

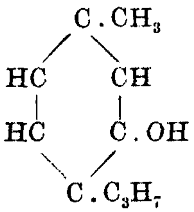
where the numbers refer to the relative position of the radicles in the benzene nucleus. Which represents ordinary apiol and which dill apiol is not yet determined. Here the C_3H_5 is the allyl group. The iso-apiols are of the same constitution, except that the C_3H_5 group represents the propenyl radicle in each case.

Diosphenol, $C_{10}H_{16}O_2$, is a constituent of the oil of buchu leaves. It was originally discovered by Flückiger. It was originally looked upon as an oxycamphor, but it is now regarded as a phenol-aldehyde. It forms colourless crystals, melting at 82° and boiling at 232°. It forms an oxime, $C_9H_{14}(OH)CH:NOH$, melting at 156°, and a phenylhydrazone, which can only be solidified at low temperatures. It shows, in fact, all the general characters of an aldehyde, as

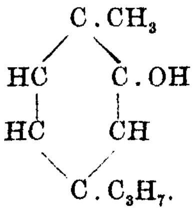
well as those of a phenol. In its latter relationship, it can be extracted from the oil with potash, and precipitated from the aqueous solution by means of an acid. Its constitution is probably $C_9H_{14}(OH)COH$, but further than this, is not definitely decided.

PHENOLS WITH TEN CARBON ATOMS.

Methyl-propyl-phenol, $C_{10}H_{13}OH$.—Of the twenty possible isomeric forms of this phenol, only two are of common occurrence in essential oils. These are *thymol* and *carvacrol*. Thymol exists in various oils, notably in that of thyme. To obtain it in a fairly pure state, the oil can be shaken with a solution of caustic potash; the aqueous layer, after separation, is treated with excess of hydrochloric acid, which precipitates the free phenol. It can also be prepared artificially from nitrocumic aldehyde. Thymol forms large, colourless crystals, melting at 44°, and boiling at 230°. It has an odour resembling thyme, and is a very strong antiseptic. On distillation with phosphorus pentasulphide it yields cymene. Carvacrol occurs in a number of oils of the thyme family, and can be prepared artificially by heating carvone, an isomeric ketone, with phosphoric acid, or by heating camphor with iodine. It is a thick oil, solidifying at 0°, and distilling at 236°. The constitutions of thymol and carvacrol are:—



Thymol.



Carvacrol.

Alcohols.

A number of the aromatic alcohols occur in small quantities in a few oils, but the two following are the most common, occurring chiefly in some of the aromatic balsams :—

Benzyl alcohol, $C_6H_5 . CH_2OH$, is the simplest alcohol of the benzene series. It is a colourless liquid, of aromatic odour, occurring in the form of esters, chiefly in the balsams of Peru and Tolu and storax. It can also be obtained artificially by several methods, such as the reduction of benzaldehyde. It boils at 206°, and has a specific gravity about 1·055 at 10°. It is only slightly soluble in water, but readily so in alcohol and ether. Amongst the more important of its esters are benzyl benzoate, a crystalline compound melting at 21°, and benzyl cinnamate, melting at 39°. Both are aromatic bodies. Oxidation of benzyl alcohol gives rise to benzaldehyde and benzoic acid.

Styryl alcohol, $C_6H_5(CH : CH . CH_2OH)$, also known as styrol or cinnamic alcohol, exists as styracine, or cinnamyl cinnamate, $C_8H_7 . CO_2 . C_9H_9$, in storax. This body melts at 44°, and when boiled with alkalies yields the free alcohol and alkaline cinnamate. The alcohol is a crystalline solid, melting at 33° and boiling at 250°. It possesses a hyacinth-like odour.

Aldehydes.

These bodies are of more frequent occurrence than their corresponding alcohols. The more important of them are benzaldehyde, salicylic aldehyde, anisic aldehyde, cinnamic aldehyde, and cumic aldehyde.

Benzaldehyde, C_6H_5COH, is the main constituent of oil of bitter almonds and other oils of the same family. It can be formed in various ways, including the oxidation of benzyl alcohol, or, as is usually done, by acting on benzal chloride, $C_6H_5CHCl_2$, with sulphuric acid or with milk of lime, or by

heating benzyl chloride, $C_6H_5CH_2Cl$, with water and lead nitrate. Artificial benzaldehyde is manufactured and sold largely as "artificial oil of almonds". It is almost identical with the natural oil, but possesses a much harsher odour, probably due to the presence of traces of impurities, which generally consist of chlorinated compounds. The natural benzaldehyde results from the decomposition of a glucoside, amygdalin, under the influence of the ferment emulsin in the presence of water (*vide* oil of bitter almonds). Benzaldehyde is a colourless liquid, of strong almond odour, of high refractive power, boiling at 179°. Its specific gravity is 1·050 at 15°. It is slightly soluble in water, and freely so in alcohol and ether. It combines to form a crystalline compound with alkaline bisulphites, and, generally, exhibits all the usual properties of an aldehyde. It is easily oxidised by the air to benzoic acid.

Salicylic aldehyde, $C_6H_4(OH)(CHO)$.—This body is an oily liquid of aromatic odour, occurring in the oils of several varieties of *Spiræa*. It can also be formed artificially by the oxidation of its alcohol saligenin, or by the action of chloroform and caustic potash on phenol. It is an oil of specific gravity 1·172 at 15°, solidifying at − 20° and boiling at 196°. It is easily reduced by sodium to its alcohol saligenin, or oxidised to salicylic acid.

Anisic aldehyde, $C_6H_4(OCH_3)(CHO)$, exists in minute quantities in oils such as aniseed and fennel. Commercially it is sold as "aubepine" or artificial hawthorn (*q.v.*). It is a colourless liquid of specific gravity 1·123 at 15°, boiling at 248°.

Cinnamic aldehyde, $C_6H_5(CH:CH.COH)$, is the chief ingredient of oils of cassia and cinnamon. It is prepared artificially in large quantities by the action of caustic soda on a mixture of benzaldehyde and acetic aldehyde, according to the equation—

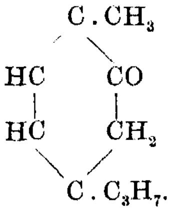
$$C_6H_5.COH + CH_3.COH = C_6H_5.CH:CH.COH + H_2O.$$

The natural oils containing cinnamic aldehyde are, however, much finer in odour than the artificial product. Cinnamic aldehyde is a colourless oil, slightly heavier than water, boiling at 247°. It combines with alkaline bisulphites to yield a crystalline compound, and possesses all the usual properties of an aldehyde. It is easily oxidised to cinnamic acid.

Cumic aldehyde, $C_6H_4(C_3H_7)(CHO)$, or cuminol, is *para*-isopropyl-benzaldehyde. It is a constituent of several essential oils, notably Roman caraway oil. It is an aromatic oil, of specific gravity ·973, boiling at 235°. It forms a crystalline compound with sodium bisulphite, by means of which it can be separated in a state of purity.

KETONES.

The only ketone belonging to this series which occurs to any great extent in essential oils is *carvone* $C_{10}H_{14}O$ (also known as carvol). This body is the important constituent of oils of caraway and dill. It is isomeric with carvacrol, into which it is easily changed by the action of caustic alkali. Its constitution is :—



It is a colourless oil boiling at 225°. It is optically active, existing in both the *dextro*- and the *laevo*-rotary forms. The optical activity is usually given as 62°, but the purest specimen from oil of caraway examined by the author had a rotation of + 58·6°, and a specific gravity ·9619. Inactive carvone can be obtained by mixing equal quantities of the optically active isomers. Carvone yields all the

usual ketonic compounds, such as the crystalline oxime and phenylhydrazone. The former compound is interesting on account of the fact that it is identical with nitrosolimonene (*vide* limonene). Carvone also forms a crystalline compound with sulphuretted hydrogen $C_{10}H_{14}(OH)(SH)$. This results by passing the gas through an alcoholic solution of caraway oil saturated with ammonia gas. The resulting crystals can be purified by recrystallisation, and decomposed by alcoholic potash, when nearly pure carvone results. The following table gives the optical rotations of the purest specimens of dextro- and laevo-carvone derivatives that have been prepared. They are chiefly from Heusler's *Die Terpene*.

	Derivatives of	
	Dextro-carvone.	*Laevo-carvone.*
Carvone	+ 62°	− 62°.
Carvone sulphydrate	+ 5·53°	− 5·55°.
Carvoxime	+ 39·71°	− 39·34°.
Benzoyl carvoxime	+ 26·47°	− 26·97°.
Benzoyl hydrochlor-carvoxime	− 10·58°	+ 9·92°.

ACIDS.

The chief of the aromatic acids found in essential oils are benzoic, salicylic and cinnamic acids. These usually exist in the form of esters, the compounds with alcoholic radicles already referred to; occasionally, however, they are found in the free state.

Benzoic acid, C_6H_5COOH, is found to a large extent in the free state in various resins, and as benzyl benzoate $C_6H_5CH_2 . CO_2 . C_6H_5$, in various essential oils. It also results from the oxidation of benzyl alcohol and benzaldehyde, and can also be prepared by numerous synthetic reactions. It forms white, shining leaflets, melting at 120°. It is readily volatile, either alone or with steam. It is but slightly soluble in water. Amongst its more important esters are methyl benzoate, $CH_3 . CO_2 . C_6H_5$, a liquid boiling at 199°; ethyl

benzoate, $C_2H_5 . CO_2 . C_6H_5$, boiling at 213°; and benzyl benzoate, $C_7H_7 . CO_2 . C_6H_5$, melting at 21°.

Salicylic acid, $C_6H_4(OH)(COOH)$, is found naturally, chiefly as methyl salicylate, which forms almost the whole of oils of wintergreen and sweet birch. Salicylic acid itself is *ortho*-oxybenzoic acid, and when pure forms crystalline prisms, melting at 155°. It is slightly soluble in cold water, but easily so in most organic solvents. The pure acid may be obtained by boiling the natural oil in which it occurs, with alcoholic solution of potash, and decomposing the potassium salt with hydrochloric acid. After purification, the acid is found to be almost entirely free from foreign bodies. It can be obtained by numerous artificial methods, the chief of which is that patented by Kolbe, or some modification of it, the patent having now expired. This consists of heating sodium phenol in a current of carbonic acid gas at 180° to 220°, when di-sodium salicylate results.

$$2C_6H_5ONa + CO_2 = C_6H_4(ONa)(CO_2Na) + C_6H_5OH.$$

The salicylic acid, liberated from this salt by means of acids, usually contains a little *para*-oxybenzoic acid, and, although modern methods of preparation and purification largely overcome this objection, the natural acid is always preferred to the artificial, and commands a higher price. The most important ester of this acid is methyl salicylate above mentioned. This body, $CH_3 . CO_2(OH)C_6H_4$, is an agreeably smelling liquid, boiling at about 226°, of specific gravity about 1·20 at 15°. The oils of wintergreen and birch consist almost entirely of this body; so that methyl salicylate, obtained by passing a current of hydrochloric acid gas into a solution of salicylic acid in methyl alcohol, is now largely sold as artificial oil of wintergreen.

Cinnamic acid, $C_6H_5 . CH : CH . CO_2H$, exists free in various resins, and to a certain extent in some essential oils. It can be prepr.red by numerous synthetic reactions, and

is now of great importance, on account of its value in the synthesis of indigo. A useful method of obtaining the acid is to boil 3 parts of benzaldehyde with 3 parts of sodium acetate and 10 parts of acetic anhydride. Water is then added, the acid dissolved in alkali, and finally precipitated with HCl and recrystallised. Pure cinnamic acid crystallises in fine needles, melting at 133°. Styracine, the cinnamic ester of cinnamyl alcohol, has already been mentioned.

V. Aliphatic Compounds.

Apart from the open-chain compounds, already described under the geraniol and citronellol group, there exist in essential oils a few bodies belonging to the open-chain or aliphatic series. The most common of these are the alcohols, aldehydes and acids belonging to the ethyl alcohol and acetic acid series. They usually exist either as the free alcohols and aldehydes, or as combinations of the alcohols and acids, as esters. For the purpose in view, the constitution and general properties of the most important of these will suffice.

Alcohols.

Methyl alcohol, $CH_3 . OH$; liquid boiling at 66°, specific gravity, ·796 at 20°, soluble in water in all proportions. It exists in the free state in traces in oil of cloves; largely in the form of esters (*vide* salicylic acid).

Ethyl alcohol, $C_2H_5 . OH$; liquid boiling at 78°, of specific gravity ·8062 at 0°, soluble in water in all proportions. It exists in small quantities in the free state in several essential oils, and also as esters.

Propyl alcohol, $CH_3 . CH_2 . CH_2OH$; liquid boiling at 97°, of specific gravity ·8044 at 20°.

Isopropyl alcohol, $(CH_3)_2CH . OH$; an isomer of the last described body, boiling at 83°, of specific gravity ·7887 at 20°.

Butyl alcohol, $CH_3 . CH_2 . CH_2 . CH_2 . OH$; liquid boiling at 117°, of specific gravity ·8099 at 20°.

Isobutyl alcohol, $(CH_3)_2 . CH . CH_2OH$; liquid boiling at 108°, of specific gravity ·8020 at 20°.

Isoamyl alcohol (isobutyl carbinol), $(CH_3)_2CH . CH_2 CH_2OH$; liquid boiling at 131°, of specific gravity ·8104 at 20°.

Hexyl alcohol, $C_6H_{13} . OH$; liquid boiling at 157°, of specific gravity ·819 at 23°.

Octyl alcohol, $C_8H_{17}OH$; liquid boiling at 191°, of specific gravity ·830 at 16°.

ACIDS.

Acetic acid, CH_3COOH; acid corresponding to ethyl alcohol, from which it can be obtained by oxidation; occurs largely in the form of esters, such as geranyl acetate, bornyl acetate, menthyl acetate, etc., in many essential oils; a crystalline solid, melting at 16·7° when absolutely pure, but liquid if it contains more than traces of water; boils at 118°, specific gravity, 1·0514 at 20°.

Propionic acid, $C_2H_5 . COOH$; liquid boiling at 140°, of specific gravity ·992.

Butyric acid, $CH_3 . CH_2 . CH_2 . COOH$; liquid boiling at 163°, of specific gravity ·9587 at 20°; found chiefly as hexyl and octyl esters.

Isobutyric acid, $(CH_3)_2CH . COOH$; liquid boiling at 155°, of specific gravity ·949 at 20°; found both in the free state and as esters.

Valeric acids, $C_5H_{10}O_2$.—Normal valeric acid does not appear to be found in any essential oils. Isovaleric acid $(CH_3)_2CH . CH_2 . COOH$, is found; it is a liquid boiling at 174°, of specific gravity ·947. Another isomer, also found in essential oils, is methyl-ethyl-acetic acid, $(C_2H_5)(CH_3) . CH . COOH$. This is an optically active liquid, boiling at 175°, of specific gravity ·941 at 21°.

Caproic acid, $C_5H_{11}COOH$; liquid boiling at 205°, solidifying at − 2°, specific gravity, ·928 at 20°. (The above-described acids are mono-basic, belonging to the acetic series.)

Tiglic and angelic acids, $C_5H_8O_2$. — These two acids are geometrical isomerides. They are unsaturated acids, belonging to the acrylic series. Tiglic acid forms crystals melting at 64·5°; angelic acid melts at 45°. The constitutions of these bodies are :—

$$\begin{array}{c} CH_3\,.\,CH \\ \| \\ CH_3\,.\,C\,.\,COOH \end{array} \qquad\qquad \begin{array}{c} CH_3\,.\,CH \\ \| \\ COOH\,.\,C\,.\,CH_3 \end{array}$$

Angelic acid. *Tiglic acid.*

These two acids occur chiefly as esters in Roman chamomile oil.

Hydrocyanic acid, HCN. — This very poisonous acid occurs in bitter almond oil, and other oils of the same family, but is frequently removed from the oil before it is used. When pure, hydrocyanic or prussic acid is a mobile liquid of specific gravity ·697 at 18°, and boiling at 26·5°.

ALDEHYDES.

Acetaldehyde, $CH_3\,.\,COH$, is the aldehyde corresponding to ethyl alcohol and acetic acid. It is a liquid of peculiar odour, boiling at 21°, of specific gravity ·8009 at 0°. It has been found in one or two oils.

Valeric aldehyde, $(CH_3)(CH_2)_3\,.\,CHO$; liquid boiling at 102°.

Isovaleric aldehyde, $(CH_3)_2CH\,.\,CH_2\,.\,CHO$; liquid boiling at 92°.

SULPHUR COMPOUNDS.

Vinyl sulphide, $(C_2H_3)_2S$, is a constituent of oil of *Allium ursinum*. It is a liquid of noxious odour, boiling at 101°, of specific gravity ·9125.

Allyl sulphide, $(C_2H_5)_2S$, is a constituent of oil of garlic, and occurs in many oils belonging to the *Cruciferæ*. It is a liquid of very unpleasant odour, boiling at 140°.

Allyl thiocyanate, $C_3H_5 . NSC$, is the principal constituent of ordinary mustard oil. It results from the decomposition of the glucoside, potassium myronate, which breaks up under the influence of the ferment myrosin in the presence of moisture, as follows :—

$$\underset{\text{Potassium myronate.}}{C_{10}H_{18}KNO_{10}S_2} = \underset{\text{Glucose.}}{C_6H_{12}O_6} + KHSO_4 + \underset{\text{Allyl thiocyanate.}}{C_3H_5 . NSC}$$

It can be obtained artificially by distilling allyl iodide or bromide with alcoholic potassium thiocyanate. Such a product is generally sold as artificial mustard oil, and it has largely replaced the natural oil. It is a foul-smelling liquid, boiling at 151°, of specific gravity 1·017 at 10°.

Other Bodies.

Methyl nonyl ketone, $CH_3 . CO . C_9H_{19}$, is the only ketone belonging to the fatty series which is found to any extent in essential oils. It occurs in oil of rue, and is a liquid of strong odour, boiling at 225°. If cooled it solidifies, and then melts at 13°.

Paraffins.—A number of solid hydrocarbons have been found in several oils, such as oil of roses, which probably are members of the paraffin series of the general formula, C_nH_{2n+2}, but at present little is known definitely of the exact chemical relationships of these bodies.

CHAPTER III.

THE PREPARATION OF ESSENTIAL OILS.

THE methods used for obtaining essential oils from the plants yielding them vary greatly, not only in principle, but also in detail. Indeed, in many cases where the principles underlying the various processes are identical, the actual details are governed by so many circumstances, that only an intimate knowledge of the chemistry of the bodies in question, coupled with a liberal practical experience, will ensure the attainment of the best results. The present chapter is devoted to a brief outline of the most important processes in general use, without devoting too much space to details, which, treated in a text book, could not yield the practical man nearly so much information as could be obtained during a short stay in a factory. Generally speaking, the processes used for obtaining essential oils may be grouped under the three headings—Expression, Distillation, and Extraction with a solvent (the latter including the various absorption processes).

EXPRESSION.

This process is only of value in those cases where the substances operated upon contain a considerable amount of oil, and are of a certain degree of softness.

In general, the principle of the process is as follows: the substance yielding the oil (the peel of the orange, lemon, bergamot, etc.), freed as much as possible from all adhering substances, such as the soft endocarp, is placed in a cloth

and subjected to great pressure. The form of the press, and the nature of the power used, will vary according to the quantity operated upon, etc. The liquid expressed from the substance is usually an opaque milky fluid, which consists of the oil, water and various solids, either dissolved in the water or held in suspension. The liquid, on standing in tall narrow vessels for a few days, separates into two layers, the oil on top and the watery fluid below. This latter generally shows division into two layers itself, the bottom one consisting of a deposit of the various albuminous and cellular substances which were held in suspension in the liquid. The crude oil is separated in the ordinary way by any mechanical appliance which will allow the liquids to be run off as in a separatory funnel. Such, for example, is a bottle with lateral taps, by which the water is first run off through a lower tap; the oil can be run off almost completely through an upper one. The oil, however, is always turbid, and requires purification, either by distillation or filtration. In the special cases mentioned distillation impairs the quality of the oil, so that filtration is resorted to. As this operation requires some time, it is of the greatest importance to exclude, as far as possible, any excess of air. This indeed is usually necessary when dealing with essential oils, for most of them are easily oxidised, and care should be taken to prevent the action of the air; and as this is accelerated by heat and light, cool dark places are usually the most suitable for storing them in. The following diagram shows the principle of a useful and simple filter which can be used for many oils. It possesses the advantage of excluding all air from acting on the oil during filtration, except that contained in the apparatus when the operation is started.

Here F is the top of a glass receiving bottle, closed by a tightly fitting cork with two holes in it. The top rim of

the glass funnel, T, is ground smooth and covered with a smooth wooden plate, D, with an india rubber ring on its lower side, and pierced by a hole in the centre. Through this hole is placed a bent glass tube, which is fitted tight into the hole by means of a rubber cork, and securely connected with the rubber tube, K. This terminates in another bent glass tube which, with the nose of the funnel, pierces the cork of the receiver. When the filter paper is placed in the funnel and this is filled with the oil, the lid is fixed on and need not be removed, except to fill up the

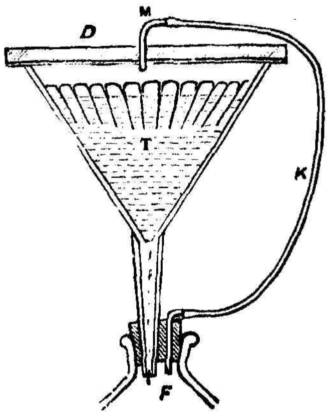


FIG. 2.

funnel again, until the receiver is full. By this means the air of the receiver is gradually driven into the funnel to take the place of the oil, and so contact with the outside air is entirely avoided.

As a matter of fact, the use of an actual press is but rarely employed in the preparation of the oils above mentioned (lemon, orange, etc.). The following processes, in which very little pressure is used, are largely employed in the preparation of this group of oils. In Sicily and the south of Italy the *éponge* or sponge method is very laagely employed.

This has been described by various writers, and probably the following description by Mr. Arthur Barrett (*Year Book of Pharmacy*, 1892, p. 505) is as accurate as any. He says: "The principle on which the extraction of the essence is carried out may be illustrated in this way. If you hold a piece of lemon peel up to the light, and turn it inside out, a fine shower of mist will be seen to be forcibly ejected. This is not all oil, but a mixture of oil and water. Most people are unpleasantly acquainted with this phenomenon, though many may not have actually seen it, for in peeling a lemon or orange with the fingers a little of the oil is often ejected into the eye, causing a considerable amount of pain. By turning the lemon peel inside out almost the whole of the essence is removed from the peel, for each little globule of oil appears to be surrounded by water, and the liquid which remains adherent to the peel consists principally of water. As it is impossible to turn every piece of peel actually inside out, the following method is adopted. One man takes a lemon in his hand, and with three rapid strokes with a large knife cuts off nearly all the peel in three slices. The central portion which is left consists of most of the pulp with a little of the peel—top and bottom. This is simply pressed for making lemon juice. The slices pass to a second workman, who sits on a low chair with a common quality bath sponge, worth about sixpence, in one hand. With the other he presses the slice of peel against the sponge, pressing the edges of the peel only with his fingers, the object being to press the convex piece of lemon peel as nearly flat as possible. The amount of pressure used is very slight, and at first sight it seems incredible that the oil globules can have been broken; but, if you try the experiment of turning this exhausted peel inside out, nothing more can be extracted. The sponge is periodically squeezed. One man working in this way can extract 1½lb. (English)

essence of lemon per day. To ensure the cells being fully charged with moisture it is usual to allow the lemons to stand in water for a short time; and I myself propose washing the lemons in a stream of running water."

The *écuelle* process, which is employed in the north of Italy and the south of France, depends on the preliminary breaking of the oil globules by means of spikes or knives, and varies in detail, according to the quantity to be operated upon. A simple *écuelle* is a saucer-shaped vessel, about 8 in. to 10 in. in diameter, usually made of copper, tinned inside, and covered inside with short spikes, about ¼ in. to ⅓ in. long. In the bottom of the saucer is a hole about ½ to ⅓ in. in diameter, leading to a hollow tube about 4 in. or 5 in. long. A fruit is placed in the vessel, and, by means of a rapid rotary motion, causes the oil cells to be broken by means of the spikes. The escaping oil flows into the hollow tube, which is periodically emptied.

In both these cases the peel is generally treated, after all the oil possible has been obtained, either by soaking in warm water or by distillation, to obtain the remainder of the oil, which is of an inferior quality, as distillation impairs the value of these oils.

An apparatus, known as the thermopneumatic extractor, has been invented by Montfalcone for the extraction of all varieties of *citrus* oils. The inventor claims that a far higher yield of oil of equal quality is obtained by the use of his apparatus, which is described as follows:—

1 is a hollow cylinder of sheet iron, the interior surface of which is studded with a large number of metallic knife-points. This cylinder revolves on two axles, attached to it at diagonally opposite points. Its capacity is such that, when charged, it is capable of holding 1200 or 1500 lemons. The cylinder having been properly charged, say with the above-mentioned number of lemons, together with a small

quantity of water, it is set in motion by aid of the shafting and pulleys, driven by the small steam-engine. The fruits are thereby made to come in contact with the metallic lancets, and their whole surface gradually becomes punctured sufficiently to cut or rupture the cells containing the essential oil, which escapes. The cylinder, 1, has double walls, the space between them being intended for the circulation of a current of steam, which is admitted to heat the water and to facilitate the extraction of the oil, while, at the same

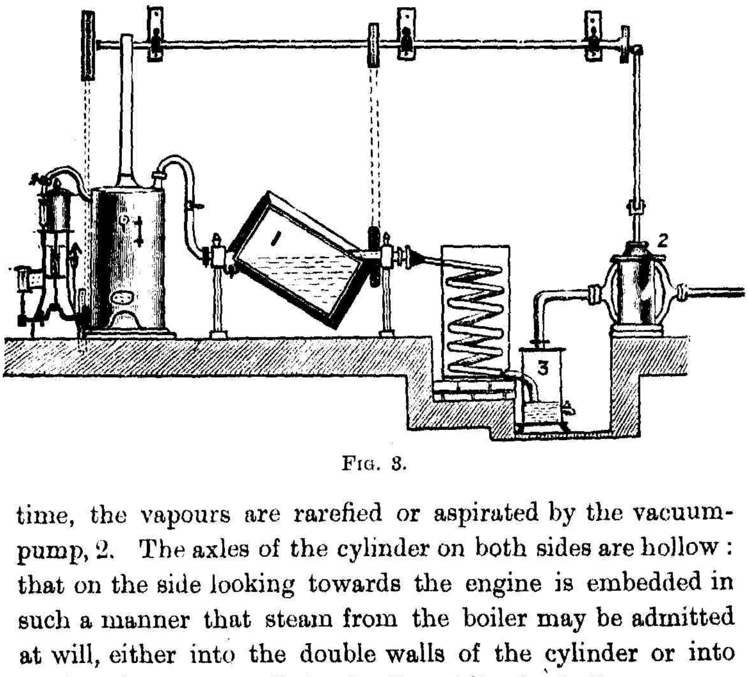


FIG. 3.

time, the vapours are rarefied or aspirated by the vacuum-pump, 2. The axles of the cylinder on both sides are hollow: that on the side looking towards the engine is embedded in such a manner that steam from the boiler may be admitted at will, either into the double walls of the cylinder or into the interior of the cylinder itself; while the hollow passage in the other axle communicates with a condensing-worm, the outlet of which descends into a cylindrical vessel, 3, intended to receive the condensed products, consisting of water and essential oil. When the apparatus is first set in

motion, the pump begins to produce a vacuum during the first revolutions of the cylinder. Steam being now cautiously admitted into the double walls of the cylinder, the water is raised to boiling at a comparatively low temperature, and the vapours charged with the essential oil rapidly pass over into the receptacle. With a two-horse-power engine and a boiler designed for a five-horse-power engine, five such machines may be driven at once, and the operation, including the time required for charging and emptying, is completed in three-quarters of an hour.

Schimmel (*Report*, April, 1896) says that lemon oil is in general manufactured in three ways:—

"1. The *Spugna* process. This is the traditional operation with sponges, as described by Prof. Flückiger in his well-known sketch, 'Easter Vacation in the South' (*Arch. d. Pharm.*, vol. iii., xxvii., p. 1065).

"2. The *Scorzetta* process. The fruits are cut into two halves, the pulp is removed with a kind of spoon, and all the parts of the peel are then pressed against a sponge by constantly turning it in the palm of the hand. This method has the advantage that the peels remain unbroken, and retain their original appearance. After they have been deprived of the oil, they are salted, and then exported under the name 'Salato'. The pulp also remains unimpaired, so that it yields its full supply of lemon juice. After having passed twice through the pressers it is used for feeding cattle.

"3. The *Machina* process. A number of contrivances have been tried for obtaining the essential oil of agrumini fruits by other less empirical and more economical methods. More recently a machine, which has a rather complicated construction but works very well, has come into use in Nizza di Sicilia, Mascali and Tremestieri. The product obtained by this process, however, is said to be less profitable, because both the quantity obtained and the quality of

the oil leave much to be desired. It must remain to more extended experience to demonstrate whether this machine will prove a success, or whether it will fall into oblivion, like most of its predecessors."

Distillation.

The majority of essential oils are obtained by a process of distillation, but the question, when treated as fully as it deserves, becomes so largely an engineering matter that no attempt is here made to deal with the *technique* of the various processes. A few words on the principles underlying the general methods adopted will amply suffice for the purpose in view. In the first place, it is to be noted that great attention has to be paid to the properties of the oils, and of their individual constituents, in deciding what treatment is most advantageous. Many compounds are decomposed by distillation, notably certain esters; others are modified by heat to such an extent, that distillation materially impairs the odour of the oil. Certain oils, obtained by other processes, are submitted to the process of distillation, or rectification, as it is then termed, and often the quality is by no means improved. This is the case with oil of bergamot, in which part of the linalyl acetate is decomposed into its constituents on distillation, and an inferior oil results.

The early process used in civilised countries, and which is still used largely by those which are less civilised, was distillation by means of an open fire. There the portion of the plant which yields the volatile oil is prepared in the most advantageous manner, and introduced into an ordinary still with the requisite quantity of water. When the fire is applied the water boils, and the steam carries over with it the essential oil of the plant. The steam carrying the oil, either in vapour itself or mechanically suspended, is condensed, and the resulting oil separated from the water in

any of the usual ways. Two disadvantages are very clearly indicated here. Firstly, the plant itself may very easily be burnt, with the result that the oil has a disagreeable empyreumatic odour; secondly, a very careful adjustment of the amount of water is necessary. Too small a quantity increases the risk of burning the plant substance, whilst too much water results in a very large distillate, and, as all oils are slightly soluble in water, a considerable quantity is lost, or at best is only recovered in the form of an aromatic water. As an example of the effects of heat, when a direct-heat still is used, the very high specific gravity and inferior quality of the native distilled sandal-wood oil in India, as compared with that distilled in England, may be quoted.

To obviate this disadvantage, the simplest modification is that used to a large extent in distilleries which turn out some of the best oil produced. This consists in suspending the plant substance in copper cages, which do not quite touch the bottom of the still. The water is run in, to the proper quantity, and when heat is applied the water boils without any danger of the plant substance being burnt. Or a false perforated bottom may be used, upon which the plants are placed. Some such modification of this is used in the distillation of various flowers in England, and, as several English oils are undoubtedly the finest the world produces, it is clear that the process used cannot be other than a good one. In such a case the body of the still should be very shallow, as compared with its width, in order to allow the oil to distil over as rapidly as possible, as otherwise the oil first carried up by the steam from the bottom of the mass of flowers would be deposited in the cooler top portion of the still, and remain there until again taken up by the rising steam. This means a longer exposure to heat, which is never advantageous to any essential oil, and certainly detrimental to one with a delicate odour.

A convenient method of preventing the plant from being injured by proximity to the fire is shown in the following diagram :—

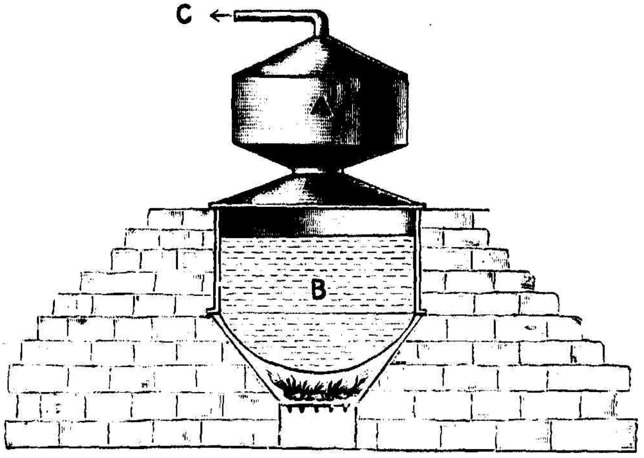


Fig. 4.

Here the plant substance is placed in the vessel, A, which has an opening, covered with wire gauze, into the steam generator, B. When the water is boiled over an open fire, the steam passes through this opening, and permeates the plant mass, carrying over the essential oil through the outlet, C, into the condensing tube.

In general, however, the process of steam distillation, in which the steam is generated in a boiler, and let, by means of a pipe, into the mass of plant substance in the still, possesses many advantages. The plant is never exposed to the danger of burning, and the minimum quantity of water is collected with the oil. To decrease the quantity of water to the minimum, it is of great advantage to maintain the plants at a high temperature, independently of the steam used for distillation. This is best effected by lining the still with a coil of pipes, through which high pressure steam passes.

By this means the mass is heated without any danger of burning, and without adding any water to it. It is then in a good condition for the steam to rapidly carry over the oil, and, in addition to the use of less water for distillation, the time taken by the process is materially shortened.

The following description of a still used by Schimmel & Co. will illustrate the use of steam, both for distillation and for the purpose of heating, as described above. The still itself is a tall, conical body, A, with a perforated false bottom, about 8 in. from its true bottom. Upon this the

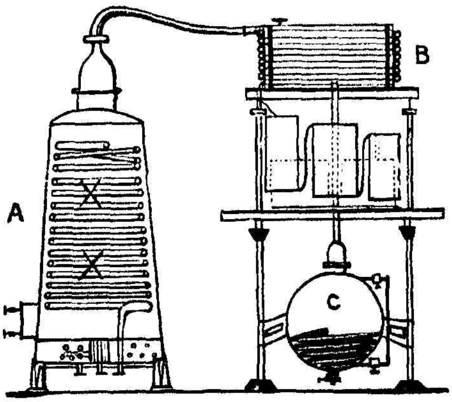


FIG. 5.

plants are placed, and immediately underneath steam enters by a pipe, which is coiled round and perforated under the false bottom. A coil of pipes, XX, having no opening inside the still, lines the whole of the interior, and through this steam is passed, which is kept at any required pressure and temperature. In the middle of the still mechanical stirrers are fixed, which materially increase the rate of distillation by continually turning over the whole mass. The steam from the bottom perforated coil traverses the whole mass, and carries over the essential oil through the outlet at the top of the still, and is condensed in the ordinary way in the

condenser B, through which it passes to a series of separators to the collecting flask C.

A further advantage is obtained especially in cases where the odour of the oil is very delicate by conducting the operation under a greatly reduced pressure. Not only can the distillation be carried on at a lower temperature, but it is much more rapid, and the quantity of water condensed is not excessive. The only disadvantage arising is the fact that a certain quantity of the oil may be lost in the vapour not condensed in the receiver, which is carried away by the exhaust pump. However in practice this is not a very serious matter. Distillation under greatly reduced pressure is largely used in the preparation of "terpeneless" oils.

Such are the principles of the processes generally employed in the distillation of essential oils. Some details will be given under special oils when treated systematically, when points of interest in connection with their preparation arise.

EXTRACTION.

All those processes by which the volatile oil is obtained by subjecting the plant substance to contact with some substance which dissolves the oil, and from which it may be afterwards recovered, may be conveniently grouped under the general heading of "Extraction". The more important of these are the following: (1) Extraction by means of a volatile solvent, which can afterwards be distilled off at a low temperature from the oil; (2) Extraction by means of a non-volatile solvent, from which the oil is recovered by dissolving it out again by means of a fresh solvent which is volatile, and does not dissolve the original solvent. The well-known process used largely in France, and termed "enfleurage," may be taken as a type of this process; (3) Extraction by means of a current of air.

Extraction with a Volatile Solvent.—The essential oils

are in general freely soluble in many organic liquids, such as ether, petroleum ether, chloroform, carbon disulphide, methyl chloride, etc. The process consists in extracting the oil by means of one of these solvents and afterwards distilling off the solvent, leaving the oil behind. There are a number of conditions essential to the successful working of this process. The solvent frequently dissolves much resin, colouring matter, etc., so that it is impossible to use the process of extraction with many plants. Consequently it is necessary to ensure that the solvent and the plant substance are so adapted that practically nothing but the oil is dissolved. In certain cases where the plant is treated in an out-of-the-way place, and distilling apparatus cannot be used, the plant is extracted with the solvent, and a mixture of oil, colouring matter and resin is obtained. On submitting this when it arrives at the distillery to steam distillation, the oil is obtained in a fairly pure condition. Again, it is necessary that the solvent should have a low boiling point, so that it can be distilled without unduly heating the oil, and without any of the oil being carried over with it. The following solvents are applicable to numerous cases:—

	Specific Gravity.	*Boiling Point.*
Carbon bisulphide CS_2 .	1·297 at 0°	47°C
Alcohol (ethyl) C_2H_5OH .	·789 at 20°	78°C
Alcohol (methyl) CH_3OH	·796 at 20°	66°C
Methyl chloride CH_3Cl .	(gas at ordinary temperatures)	– 24°C
Chloroform $CHCl_3$ . .	1·5008 at 15°	61°C
Acetone $CO.(CH_3)_2$ . .	·792 at 20°	56·5°C
Petroleum ether . .	·626 to ·700	37°-99°C
Benzene C_6H_6 . . .	·899 at 0°	80·5°C
Ether $(C_2H_5)_2O$ . .	·736 at 0°	35°C

The simplest process of extraction is merely an adaptation of the ordinary method of percolation, or, with a view to economise the solvent used, an apparatus on the principle of the ordinary Soxhlet tube is used. The chief point to be noted is the arrangement of the apparatus so that the minimum

quantity of the volatile solvent shall be lost. Various patents have been taken out in respect of extraction processes, amongst them being several involving the use of the very volatile solvent methyl chloride. One of these is well illustrated in the *Pharmaceutical Journal* (3), xiv., p. 44. Most of these are very complicated as regards the arrangement of vessels and pumps, but a simple process, in which methyl chloride is used, is described by Blogg in his evidence given before the Royal Commission of Inquiry into the vegetable products of Victoria. A jacketed vacuum still, fitted with the pump and condenser, a closed macerating vessel and a receiver are all the apparatus necessary. The fresh flowers, for it is nearly always fresh flowers that are treated in this way, are placed in the macerating vessel, which is filled up with pure methyl chloride and kept tightly fastened for a quarter of an hour. The liquid is then rapidly transferred to the vacuum pan, this is warmed and the exhaust pump is started. The solvent is rapidly evaporated, leaving the extracted oil, etc., in the pan. Great care must be exercised to see that the methyl chloride is as pure as possible. Much of the commercial product is manufactured from the trimethylamine obtained by destructively distilling the residues obtained from crystallisation of beet sugar. To purify it it is best to pass it through hydrochloric acid, and then to dry it with calcium chloride. It is then compressed into iron cylinders, when it forms a mobile liquid. To purify oils obtained by such processes it is necessary either to dissolve them out with alcohol from the wax, etc., which is extracted with them from the plants, or to purify them by a process of rectification (distillation). Extraction with a solvent in the cold may be accelerated by fixing the vessel containing the solvent at a much higher level than the percolator. These are connected by a vertical pipe, the connections being made perfectly tight, with the result that the pressure of the liquid on the substance

to be extracted is greatly increased, and the process is thereby much accelerated.

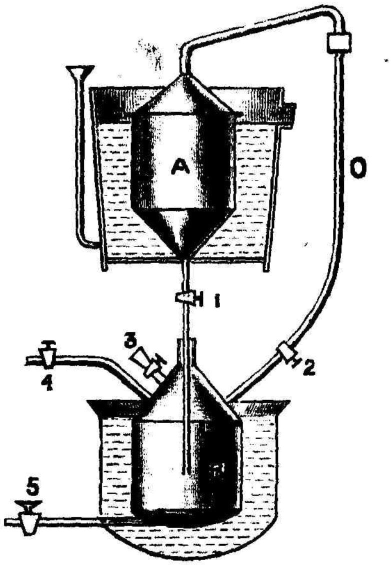


FIG. 6.

The above diagram represents a simple apparatus for extraction on the Soxhlet principle. The flowers to be extracted are placed in the vessel A, immersed in a tank of cold water, and the solvent is placed in the vessel B, immersed in a tank of warm water. When the connections have been made all the taps except 1 and 2 are closed, and the water in the tank surrounding B is heated sufficiently to make the solvent boil. This passes up the tube O and enters the vessel A, where it condenses and penetrates through the mass of flowers, finding its way back to B through the vertical tube. The solvent is again evaporated, leaving the extracted oil in B, thus making the process continuous. When exhaustion is complete, taps 1 and 2 are turned off, and tap 4 is turned on. The solvent is then evaporated and

passes through this tap to a condenser, and finally the residual oil is run off through the lowest tap. Any fresh supply of solvent necessary is poured into B through the funnel 3.

Extraction with a Non-Volatile Solvent.—The processes known as maceration and enfleurage are types of this method. The former is used in certain parts of France in the following manner. A quantity of a pure neutral fat such as olive oil or lard is placed in a pan heated by a water bath. The freshly gathered flowers are thrown in and left there twelve to forty-eight hours, as the case may be. The whole is frequently stirred. When the odour is entirely gone from the flowers, the fat is strained off into a fresh pan, and another lot of fresh flowers is thrown in. This operation is repeated a dozen or more times, until the pomade, as it is called, usually having a fine solid fat such as pure lard for its basis, is sufficiently strong. It is found that the odour is invariably the most delicate when the flowers have remained for the shortest time in contact with the fat. Various devices are employed in order to reduce the time of maceration, amongst which one deserves especial notice. This consists of a reservoir, containing the fat heated to about 65° or 70° C, from which it flows in a slow stream through the macerating chamber, a long tank in which wire cages of flowers are suspended in open compartments. Every now and then the basket nearest the oil reservoir is emptied and taken out, and all the other baskets moved on one compartment, a fresh basket of flowers being added at the other end. A constant movement of the oil and the flowers in opposite directions is thus ensured, and the time of maceration is materially reduced.

The oily solution has then to be treated in order to obtain the perfume from it. If olive oil has been used, it is well shaken repeatedly with pure alcohol, which after a time

dissolves out nearly all the volatile oil, from which it can either be separated by careful distillation, or it can be used directly as a perfume. If a solid fat such as lard has been used, it is necessary to cut it up into very small pieces, or mechanically divide it in some other way, in order to expose the largest possible surface to the action of the alcohol. The French process of enfleurage is used in those cases where the flowers possess so delicate an odour that the oil would be damaged by the application of heat. The process is tedious and expensive, and the yield from the flowers is always small. Hence the high price of perfumes obtained by this process. A series of rectangular wooden frames, about 2 ft. × 3 ft., with a square of strong glass fitting in their inner rims, known as "chassis," are laid one upon another to form a pile. On each is spread a very thin layer of pure neutral fat. About six to eight ounces are used for each frame. The fresh flowers are then spread upon these and allowed to remain for a period of from a half to three days. When the flowers have lost their odour, fresh ones are spread out in their place, until the fat acquires a very strong odour. *Chassis à huile* are frames provided with wire netting on which cotton or linen cloth soaked in olive oil is spread. The whole process, until the fat or oil is saturated with the odorous oil as far as is desired, takes two to three months. The fat is then removed from the glass, or the oil pressed from the cloths by a hydraulic press, and can either be used as *pomades*, or can be treated with alcohol to extract the perfume.

The process of absorption can be carried out more rapidly by arranging a series of *chassis* so that air can be drawn through the apparatus, to pass successively over all the plates. The flowers are then not placed on the fat at all, but in a separate vessel connected by a pipe to the box containing the *chassis*. Air is then drawn through the

flowers, and over the layers of fat, which absorb practically the whole of the perfume, without ever coming into actual contact with the flowers. One great advantage of this process is that the fat is less liable to become rancid than it is when placed in contact with the fresh flowers. A current of carbonic acid gas is sometimes used, in order to prevent the possibility of oxidation by means of the air.

A current of hot air is sometimes used to extract the perfume from flowers which are not too delicate to stand the treatment. But as the hot air rapidly dries up the plant, and hinders it yielding up the remainder of its volatile oil, it is necessary to ensure the air being saturated with moisture before it reaches the flowers. This is best effected by allowing it first to pass through a series of wet sponges. The air, after passing over the flowers, passes through a flask containing carbon bisulphide, or some other solvent with a low boiling point, which absorbs the oil from the air, and from which it is easily recovered.

The following table, giving the average yield obtained from the most common of the essential oils, is based on the statements of Messrs. Schimmel & Co., Leipzig.

Plant.	Per cent.	Plant.	Per cent.
Ajowan (seed)	3 to 4	Eucalyptus oleosa	1·25
Allium (plant)	·007	— staigeriana	2·5 to 3·7
Angelica (fruit)	1 to 1·2	Fennel (fruit)	1 to 6
— (herb)	·02	Galbanum (resin)	14 to 22
Angostura (bark)	1·5	Geranium (herb)	·18
Anise fruit, Chili	1·9 to 2·6	Ginger (rhizome)	2 to 3
— — Italian	2·7 to 3·5	Hop (flowers)	·3 to 1
— — Mexican	1·9 to 2·1	Hyssop (herb)	·3 to ·9
— — Prussian	2·4	Jaborandi (leaves)	·4
— — Russian	2·4 to 3·2	Juniper (berry)	·6 to 1·5
— — Spanish	3	Lavender (flowers)	variable
— — Syrian	1·5 to 6	Lemon (peel)	variable
— — Thuringian	2·4	Linaloe (wood)	...
Arnica (flowers)	·04 to ·07	— Guiana	1
— (root)	·5 to 1	— Mexico	7 to 9
Asafœtida (resin)	3·3 to 3·7	Lovage (herb)	·1 to ·2
Bay (leaves)	2·3 to 2·5	— (fruit)	1 to 2
Bergamot (peel)	variable	— (root)	·3 to 1
Bitter almonds	·5 to 1	Mace (arillus)	4 to 15
Buchu (leaves)	1 to 2	Mandarin (peel)	variable
Calamus (herb)	·2	Marjoram (herb)	·3 to ·9
Camphor (leaves)	1·85	Matico (leaves)	1 to 3·5
— (wood)	4	— (leaves and flowers)	3·5 to 5·5
Canella (bark)	·7 to 1	Mignonette (flowers)	·002
Caraway (fruit)	3 to 7	Mint (*arvensis*)	·22
Cardamoms (fruit)	2 to 8	Mustard (seeds)	variable
Cascarilla (bark)	1·5 to 3	Neroli (flowers)	·1
Cassia (leaves)	·54	Nigella (seeds)	·5
— (buds)	1·9	Nutmeg (fruit)	8 to 15
— (flower stalks)	1·7	Onion (herb and bulb)	·004
— (bark)	1·2	Orange (peel)	variable
— (twigs)	·2	Origanum (herb)	2 to 3
Cedar (wood)	2·5 to 4·5	Parsley (fruit)	2 to 6
Celery (herb)	·1	Patchouli (leaves)	1·5 to 4
— (fruit)	2·5 to 3	Pennyroyal (leaves)	3
Chamomile (flowers)	...	Pepper (fruit)	1 to 2
— German	·1 to ·3	Peppermint (herb)	·1 to 1·5
— Roman	·8 to 1	Pine (needles)	·1 to ·8
Cinnamon (bark)	·5 to 1	Rose (flowers)	·02
— (leaves)	1·8	Sage (leaves)	1·5 to 2·5
Citron (peel)	variable	Sandalwood	1·6 to 5
Citronella (grass)	variable	Sassafras (root bark)	7 to 8
Clove (buds)	15 to 18	Savin (twigs)	4 to 5
Copaiba (balsam)	40 to 80	Spearmint (herb)	·3
Coriander (fruit)	·2 to 1	Spike (herb)	variable
Cubeb (fruit)	10 to 18	Staranise (fruit)	5
Culilaban (fruit)	3·5 to 4	Storax (balsam)	·4 to 1
Cumin (fruit)	2·5 to 4	Tansy (herb)	·1 to ·3
Damiana (leaves)	·9 to 1	Thuja (leaves)	·5
Dill (fruit)	2 to 4	Thyme (herb)	·3 to 2·6
Dittany (herb)	·7	Turpentine (French)	16
Eucalyptus (leaves)	...	Valerian (root)	·5 to 1
— amygdalina	3·3	Veti-vert (root)	·4 to ·9
— citriodora	1 to 4	Wintergreen (true)	·75
— dealbata	2·7	— (sweet birch)	·6
— globulus	·8 to 3	Wormseed (fruit)	1
— odorata	1·4	Ylang Ylang (flowers)	very small

CHAPTER IV.

THE ANALYSIS OF ESSENTIAL OILS.

In general, the analysis of essential oils merely involves the application of the ordinary principles of analytical chemistry to this special group of bodies, which possess many features in common. Of course many special processes have to be used in certain cases, to which attention will be drawn where necessary. The present chapter will be devoted to the details of a few methods which are in very common use in the analysis of these bodies, and which are absolutely necessary in order to form an opinion on the purity of very many oils. Particular processes will be mentioned as required. These remarks may be prefaced by saying that the obtaining of the results of an analysis is not always as difficult a matter as the interpretation of the same when obtained.

Specific Gravity.

The first thing to be done in examining an essential oil is to determine its specific gravity. For this purpose hydrometers are useless. Approximate accuracy is useless in this work, and hydrometers are only capable of yielding approximate results. For ordinary work a specific gravity bottle is generally used, holding either twenty-five or fifty cubic centimetres. There are two points to be noted in connection with this. The graduated bottles sent out by apparatus firms seldom contain the exact quantity they are supposed to do. It is therefore advisable to check the contents of the bottle, and to use the necessary correction when cal-

culating a specific gravity. Secondly, the counterpoise of a 50 cc. bottle should be about sixty milligrammes less than its apparent weight when empty on account of the air contained in the bottle. A consideration of the laws of hydrostatic pressure will show that if this be not so the specific gravity as determined will be the ratio

$$\frac{\text{weight of oil} - \cdot 06 \text{ gramme}}{\text{weight of water} - \cdot 06 \text{ gramme}}$$

instead of the correct ratio

$$\frac{\text{weight of oil}}{\text{weight of water}}.$$

This correction of ·06 gramme is not absolutely accurate, but is sufficiently so for all practical purposes.

It is essential that great care should be taken that the temperature be accurately determined when taking the specific gravity. The bottle filled with oil takes some time to assume the exact temperature of the water in which it is immersed, especially if these differ much at first. Hence it is always advisable not to depend only on an observation of the temperature of the water, but to use a very small bulbed thermometer, with which the actual temperature of the oil itself in the bottle can be taken. Specific gravities are usually expressed as the ratio of the weight of a volume of the oil to that of an equal volume of water, both at 60° F., or approximately 15·5° C. This is written $\frac{d15{\cdot}5^\circ}{d15{\cdot}5^\circ}$. Any variation in temperature can thus easily be expressed. For example, the specific gravity of, say, otto of roses at 30°, as given in the British Pharmacopœia, may reasonably be interpreted as $\frac{d30^\circ}{d15{\cdot}5^\circ}$, or as $\frac{d30^\circ}{d30^\circ}$, that is, with the water to which it is compared at 15·5° or at 30°. Wherever the specific gravity of an oil is referred to in this work, it is to be understood as referring to $\frac{d15{\cdot}5^\circ}{d15{\cdot}5^\circ}$, except when otherwise quoted.

light it will be desirable to briefly illustrate the fundamental principles upon which their application depends. Ordinary light consists of transverse vibrations in numerous planes in which is no polarity or *two-sidedness*, if the expression is justifiable; whilst plane polarised light consists of vibrations in one plane only. This may be roughly illustrated in the following manner. If a string, fixed at its ends, be plucked it will vibrate in a certain plane dependent on the direction of the plucking. If the string be passed through a slit, just wider than it is itself, in a piece of cardboard, so that the slit is in the direction of the vibrations, these will not be interfered with; but if the slit be turned round, the vibrations will be interfered with, and when it is at right angles to the direction of the vibrations, they will be totally suppressed. Light waves (for convenience, the expression, a ray of light, is more general) may be plane polarised in several ways, so that the vibrations in the one plane may be similarly interfered with, and upon this depends the use of the polarimeter. This instrument, of which the theory is described a little more fully in the footnote,[1] is constructed on several different

[1] The theory of the half-shadow polarimeter is, briefly, as follows. The light, of approximately constant refrangibility, falls on the polarising Nicol's prism, which is a rhomb of calc-spar cut obliquely by a plane perpendicular to the principal section. The cut faces are polished and cemented together again by a thin film of Canada balsam. Calc-spar is a doubly refracting substance, and in the ordinary way the incident ray is divided by the spar into two rays, the ordinary and the extraordinary, the former following the ordinary laws of refraction, the latter behaving abnormally. Two rays, then, will be found to emerge. But the refractive index of the balsam is greater than that of the spar for the extraordinary ray, and less than that for the ordinary ray, both of which are plane polarised. According to the usual laws of refraction, total reflection can only occur in passing from a more to a less refracting medium. Hence the extraordinary ray will always be transmitted, but by arranging the angle of incidence properly the ordinary ray can be totally reflected. Hence only the extraordinary ray now falls on to the Laurent plate, and it is in a plane polarised condition. This plate is made of quartz or gypsum over one half of the field, and plain glass over the other. It is a doubly refracting substance and refracts the incident ray as

principles, of which by far the most useful for all general purposes is the Laurent half-shadow instrument. In the annexed diagram, A is a small telescope, B is a magnifying glass used to read the graduation on the dial and vernier, C is one of the verniers, D is a dial graduated to half degrees, E is the analysing Nicol's prism (a specially prepared prism

ordinary and extraordinary rays. The thickness is so adjusted that it introduces a retardation of $\frac{1}{2}\lambda$ (where λ is the wave length of the light used) between the two rays. Consequently, the light emerges plane polarised from the crystalline plate, but the planes of polarisation of the rays emerging from the two halves will be inclined at an angle 2α, if α is the inclination of the incident single polarised ray to the optical axis of the quartz. Hence when this plate, with its two polarised rays, is viewed through the analysing Nicol, the two halves will be in general unequally illuminated, except when the principal plane of the Nicol be parallel to the optical axis of the crystalline plate. In this position we have the zero point of the instrument. The insertion of an optically active liquid destroys this condition by rotating the plane of polarisation, and the angle through which it is necessary to rotate the analyser in order to restore the "equal shadows" measures the rotation of the plane of polarisation.

Another simple instrument known as the *Biquartz* polariser depends on a rather different principle. Here two semicircular plates of quartz are placed in juxtaposition, each cut at right angles to its axis, one possessing *dextro-* and the other *laevo*-rotatory power. The two plates are of the same thickness, and produce equal rotations in opposite directions. The incident light in this case is white, and the lights of different refrangibilities are rotated through different angles. Hence when viewed by an analysing Nicol, waves of different refrangibilities will be quenched in the two halves, and they will in general appear of different colours. When the principal plane of the analyser, however, is parallel to the direction of the incident vibrations, the two halves will always be of the same colour, dependent on the complementary colours which are quenched. By suitably adjusting the thickness of the plate, the brilliant yellow may be quenched, and the delicate gray-violet tint, known as the tint of passage (Biot's *teinte sensible*), appears when both halves have the same colour. This point, the zero point of the apparatus, is easily fixed, for the slightest rotation to the right or left renders one half of the field blue and the other red. Having set the instrument, it is found that when an optically active substance is introduced, the tint of passage disappears, and the analyser must be rotated in order to restore it, according to the optical activity of the substance.

To most observers it is easier to obtain equal illumination in the two halves of the field than to correctly obtain the tint of passage, hence the popularity of the former apparatus.

of calc-spar, capable of polarising light) which is fixed to the graduated dial and telescope, F is the groove in which tubes containing the liquids to be examined are inserted, H is a pointer attached to the polarising Nicol's prism, G is the fixed Laurent plate (*vide infra*), and J is a plate of bichromate of potassium.

This apparatus can only be used with sodium light, as for quantitative results light of definite refrangibility must be used. A Bunsen lamp of convenient construction, into the

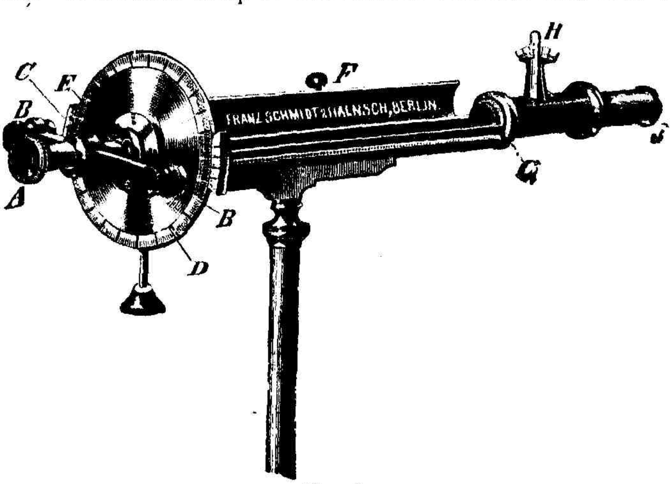


Fig. 8.

flame of which a little common salt can be introduced on a platinum wire, is placed about 4 or 5 inches from the end J. The light is further sifted by means of the bichromate plate, so that light approximately corresponding to the D line of the spectrum falls on to the polariser, and that which passes through is plane polarised. The plate G is a special contrivance, half of which is made of quartz or gypsum, and the other half of plain glass; the thickness of this is carefully graduated, and the result—the optical theory of which need not here be discussed—is that when the analyser is in a cer-

tain position with reference to the polariser and plate, the two halves of this plate appear equally illuminated. By adjusting the prisms by means of the movable pointer, H, and the screw, E, which govern the delicacy of the instrument, the zero marks on the dial and on the vernier are made to correspond when the position of equal illumination is attained. A slight rotation of the analyser in either direction by means of the projecting screw handle at once causes the two halves of the field to become unequally illuminated. Having set the instrument at zero, a tube containing an optically active liquid is inserted in the groove, F. It will now be found that the analyser has to be rotated a certain number of degrees either to the right or the left in order to restore the position of equal illumination of the two halves of the field. This is the angle through which the plane of polarisation has been rotated. The beginner will find a little difficulty in using this instrument; for example, when examining oils with high rotations or when the dial has been rotated too far, and has been taken beyond the range of sensitiveness; half an hour with some one who understands the instrument will explain its use far better than pages of printed matter. The rotation of the dial in the direction of the movement of the hands of the clock, as the observer sees it, is conventionally termed dextro-rotation, and conversely. In general, the *optical rotation* is expressed for a column of 100 millimetres. The specific rotary power is a different figure, it is expressed by the symbol $[\alpha]$, and, taking the decimetre as the unit of length for this purpose, is the observed rotation in the decimetre tube divided by the specific gravity of the liquid. The molecular rotation refers of course only to pure compounds and not to mixtures, and need not be discussed here, otherwise than to mention that it is the product of the specific rotary power and the molecular weight. In the sequel, the optical rotation will be understood to refer to the rotation

produced by a column 100 millimetres long, unless otherwise mentioned.

MELTING AND SOLIDIFYING POINTS.

Many oils possess the property of becoming solid at temperatures slightly below the ordinary, and a determination of the solidifying or melting points becomes an important criterion of purity in these cases. The melting point is not usually the same as the solidifying point, on account of the peculiar properties of bodies, included under the term superfusion, etc. In addition, the temperature recorded differs somewhat with the method used in the determination. For general work the following apparatus gives the best results in a convenient manner.

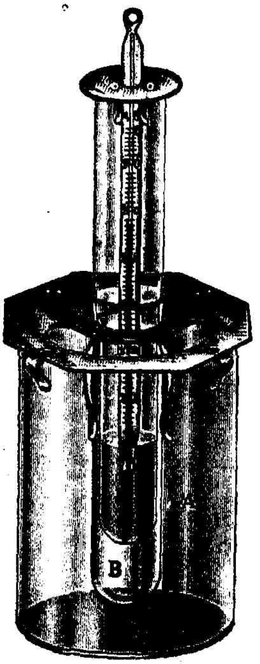


FIG. 9.

Here the outer vessel contains a sufficient quantity of the freezing mixture, such as a mixture of ice and salt, or a solution of one of the usual salts. The longer test tube acts as an air cover to the inner tube in which the thermometer is placed. A small quantity of the oil—just enough to cover the bulb of the thermometer—is placed in this tube, and in certain cases the platinum stirrer is used. The melting point is determined by freezing the oil and then removing the freezing mixture and allowing the temperature to rise slowly, and noting the temperature at which liquefaction takes place. The solidification point is determined by cooling the oil down without disturbing it until the temperature is clearly below the point of solidification. A slight agitation of the stirrer will now usually induce solidification, if not, the introduction of a crystal of the compound solidifying—anethol, for example, in the case of aniseed oil—will do so. A disengagement of heat occurs on solidification, which causes the thermometer to rise. The maximum reading during the process of solidifying may be regarded as the solidifying point.

Boiling Point and Distillation.

The determination of the temperature at which an oil begins to boil is often of importance, as is also the percentage of the oil which distils within definite limits of temperature. The results obtained in distillation processes must however be interpreted very carefully, as the *quantitative* results depend so largely on the exact conditions of distillation. For ordinary purposes, an ordinary Wurtz flask is useful for determining the temperature at which the liquid first boils, but when an examination of any of the fractions or any estimation of the quantity boiling between given temperatures is needed, a fractional distillation flask is better. These flasks are illustrated on the next page.

It is often advisable to distil or fractionate an oil under reduced pressure, especially when the constituents decompose when boiled at atmospheric pressures.

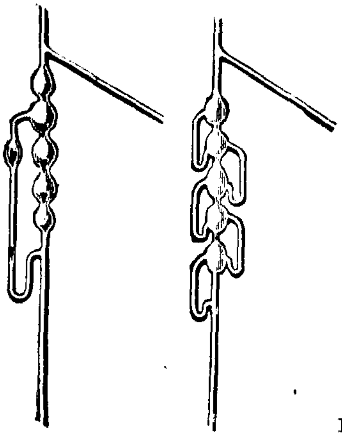


FIG. 10. Fractionating Columns.

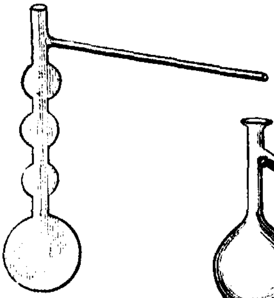


FIG. 11. Fractionating Flask.

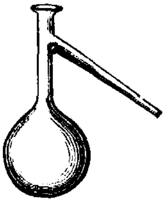


FIG. 12. Wurtz Flask.

QUANTITATIVE ESTIMATIONS OF CONSTITUENTS.

Very frequently it is necessary to make a quantitative determination of one or more of the bodies occurring in an essential oil. The methods used in these cases are of course exceedingly numerous, and in the present paragraph only a few of the most typical and generally employed, will be referred to. It should be understood, however, that these quantitative methods, as applied to complex organic mixtures, are not nearly so exact as quantitative methods of inorganic analysis, but being worked in a uniform and definite method, the results are always strictly comparable.

The Determination of Esters.—Esters, or salts of alkyl radicles, such as linalyl acetate, etc., are frequently the most important constituents of essential oils. Their importance is especially noteworthy in such cases as lavender, bergamot, peppermint and wintergreen oils, and their estimation is

very frequently necessary. The principle upon which this depends is the fact that most esters are decomposed by solution of caustic alkali (preferably in alcohol) according to the equation—

$$\text{R}\bar{\text{A}} + \text{KOH} = \text{R.OH} + \text{K}\bar{\text{A}}$$

where R is the alkyl, and Ā the acid, radicle.

To use this principle for the estimation, from 1 to 5 grammes of the oil, according to the magnitude of its ester content, are exactly weighed into a small flask capable of holding about 150 to 250 c.c., and from 10 to 25 c.c. of solution of caustic potash in alcohol are added. The strength of this should be approximately half-normal. The whole is then boiled in the water bath under a reflux condenser for from one to two hours. It is then diluted with water and the excess of potash is estimated by titration with semi-normal sulphuric acid, using phenol-phthalein as an indicator. To determine the amount of potash originally employed, it is best to perform a blank experiment with the same quantity of potash solution, merely omitting the oil, so that the blank and the oil have been treated in an exactly similar way. The difference in the two titrations gives the amount of potash used in decomposing the esters. If any free acids are present these will have neutralised some of the potash, and it is then necessary to determine by a preliminary titration how much is used for this purpose, and to deduct the result from the total quantity of potash used. The potash number is easily calculated to any desired ester from the equation given above, or, generally, from the formula—

$$x = \frac{\text{M} \times \text{N}}{10\text{W}},$$

where x is the percentage of ester, M is the molecular weight of the ester, N is the number of cubic centimetres of *normal* potash solution used for decomposing the esters, and W is the weight in grammes of the oil saponified.

The Determination of Free Alcohols.—Many oils contain large quantities of free alcohols, such as geraniol or linalol. The only generally convenient way of estimating these depends on the conversion of the alcohols into their acetic esters, and then saponifying these in the manner just described. From 10 to 20 grammes of the oil (spike, sandal-wood and geranium are typical) are boiled under a reflux condenser for one to two hours with an equal volume of acetic anhydride and 10 per cent. of their weight of anhydrous sodium acetate. After the liquid has cooled, it is diluted with water and allowed to stand in the water bath for a few hours in order to decompose the excess of acetic anhydride. The liquid is then transferred to a separator and repeatedly washed with distilled water until the wash water is perfectly neutral in reaction. The oil is then separated and the last traces of water removed by digestion with ignited sodium sulphate. About 1 to 3 grammes, depending on the alcohol content of the acetylated (esterified) oil, are then saponified as described above. The amount of *ester* in the *acetylated* oil is easily calculated, but to convert this into the percentage of *free alcohol* in the original oil requires a more tedious calculation. The following formula can be used for this :—

$$x = \frac{N \times M}{10(W - \cdot 042\,N)},$$

where x is the percentage of the alcohol in the *original* oil, M is the molecular weight, and N is the number of c.c. of normal alkali used, and W the weight of the *acetylated* oil. Here the factor ·042N is on account of the increase of the weight due to acetylation. This formula is only true if the original oil contains no esters. In cases where esters and alcohols occur together the best method is to—

(1) Estimate the esters in the original oil by a preliminary saponification of a small quantity.

(2) Saponify about 20 grammes and separate the resulting oil, which now contains all the alcohols in the free state.

(3) Estimate the total alcohols in 2 by the acetylation process.

(4) Calculate the total alcohols in the original oils from 3, by allowing for the decrease in weight of 1 when saponified.

(5) Deduct the alcohols combined as esters from the total alcohols, which gives the amount of free alcohols.

In these estimations it is necessary to calculate all the esters and all the alcohols to one formula, expressing the result, for instance, as menthyl acetate, although as a matter of fact small quantities of the corresponding propionate and butyrate may also be present, which it is impossible to estimate separately.

Absorption Processes.—Numerous constituents of essential oils, which are themselves insoluble in water, or practically so, readily form soluble compounds with certain inorganic bodies. Such, for example, are many aldehydes, which form soluble compounds with a solution of sodium bisulphite $NaHSO_3$, and phenols such as eugenol, which forms a soluble salt with potassium hydroxide. Upon this principle depend the quantitative absorption processes which are frequently used in the examination of essential oils.

The most useful method of determining the absorbable constituents is as follows. From 5 to 10 c.c. of the oil are measured carefully into a flask capable of holding about 200 c.c., having a long narrow neck graduated into $\frac{1}{10}$ c.c. Excess of the absorbing solution—in the case of cassia oil, for example, hot nearly saturated solution of sodium bisulphite, in the case of oil of cloves, aqueous solution of potash—is then added and the whole is well shaken and allowed to stand for a time. Water is then added to nearly fill the flask and the whole is allowed to stand in the water bath until any crystals formed are dissolved, and the oily layer of

unabsorbed residue rises to the surface. More hot water is carefully poured in, and the oily layer forced up into the graduated neck, when its volume is read off. Two precautions must here be taken. Firstly, the temperature at which the oil is first measured, and that at which the unabsorbed residue is measured, must be identical. Secondly, it must be remembered that the measurements only give the volume percentages, hence to determine the percentage by weight it is necessary to know the specific gravity of the oil and of the non-absorbable residue. Of course, the latter can be separated and weighed, but the advantages of this are more than counterbalanced by the loss in weight experienced whilst removing the last traces of water.

In the processes mentioned above, it must be remembered that the actual results are only approximate. For example, there is a certain small amount of potash used in the ester process, by action on bodies which are not esters but which are readily susceptible to the action of so strong a body as caustic alkali. But the whole of the potash used is calculated to esters, which will, in general, then, be returned a trifle too high. The action of acetic anhydride, too, is powerful, and it is probable that in very few, if in any, cases does the reaction take place in the simple theoretical manner, upon the assumption of which our calculations are based. Again, in absorption processes, errors arise either by secondary reactions taking place, such as when citral is absorbed by bisulphite of sodium solution, or by the incomplete absorption of the absorbable body, or, lastly, by the solution of small quantities of the non-absorbable bodies. In oil of cloves, where the eugenol is estimated by absorption by caustic potash, if the solution of potassium eugenol be separated off and extracted with ether, it is possible to obtain small quantities of the sesquiterpene, caryophyllene, which have been dissolved by the potassium eugenol solution. The

reader's attention is drawn to these facts, not with a view to depreciate the processes, which are amongst the most important of all those used in the examination of essential oils, but to accentuate the fact that the estimation of, say, citral in lemon-grass oil, or santalol in santal-wood oil, are not quite the same thing as the estimation of the majority of inorganic bodies, where determinations can frequently be depended on to $\frac{1}{10}$th per cent.

There are, of course, numerous other quantitative processes having great value in the examination of essential oils, but these will be referred to in the sequel as occasion requires.

CHAPTER V.

SYSTEMATIC STUDY OF THE ESSENTIAL OILS.

Two methods of classification of the essential oils are feasible: either by grouping them according to the identity or relationships of their constituent compounds, or according to the botanical relationships of the plants yielding them. The latter method will be followed in this work, and it will be seen that, although numerous exceptions occur, the oils from plants of the same family very frequently contain the same compound as their preponderating constituent. Probably nearly every odoriferous plant contains an essential oil, in many cases, of course, only in minute quantities, but of course only a limited number have been separated or examined. In the present chapter, the chief of those which have received attention at the hands of chemists will be described, and details of their properties and constituents given as fully as space will allow. The accompanying botanical groups are embraced in this description (p. 97).

OILS OF THE GYMNOSPERMS.

Amongst the numerous families of this widespread natural order, the pines, firs, larches, cedars, cypresses and junipers are perhaps the best known. Most of them yield essential oils from the leaves, fruit and wood, the latter also

- GYMNOSPERMS - - *Natural Order* - - Coniferæ
- ANGIOSPERMS
  - *Monocotyledons* — *Natural Orders.*
    - Gramineæ
    - Aroideæ
    - Liliaceæ
    - Iridaceæ
    - Zingiberaceæ
  - *Dicotyledons* — *Natural Orders.*
    - *Monochlamydeæ*
      - Piperaceæ
      - Urticeæ
      - Myricaceæ
      - Salicineæ
      - Chenopodiaceæ
      - Laurineæ
      - Myristiceæ
      - Euphorbiaceæ
      - Cupuliferæ
      - Santalaceæ
    - *Gamopetalæ*
      - Labiatæ
      - Verbenaceæ
      - Convolvulaceæ
      - Jasmineæ
      - Ericaceæ
      - Valerianeæ
      - Compositæ
      - Caprifoliaceæ
    - *Polypetalæ*
      - Umbelliferæ
      - Myrtaceæ
      - Rosaceæ
      - Leguminosæ
      - Saxifragaceæ
      - Hamamelideæ
      - Terebinthaceæ
      - Geraniaceæ
      - Tropæoleæ
      - Rutaceæ
      - Zygophylleæ
      - Meliaceæ
      - Simarubeæ
      - Burseraceæ
      - Tiliaceæ
      - Malvaceæ
      - Ternstrœmiaceæ
      - Clusiaceæ
      - Dipterocarpeæ
      - Polygalaceæ
      - Cruciferæ
      - Resodaceæ
      - Turneraceæ
      - Cistineæ
      - Ranunculaceæ
      - Magnoliaceæ
      - Anonacæ

frequently yielding large quantities of resin. Of these the following are the best known, and many of them are in very common use:—

I. Wood Oils.

Cedar Oil.—The oil usually known as cedar oil or cedar-wood oil is obtained by distillation of the wood of *Juniperus virginiana*, one of the family of the *Cupressineæ*. Other cedar-wood oils are occasionally met with, and will be mentioned later, but the present remarks apply to the above-mentioned oil.

The oil is generally distilled from the waste shavings from lead pencil manufacture, which are usually plentiful when the pencils are cut from logs. When thin sawn boards are imported and used, the refuse is much smaller in amount, and the price naturally rises. The yield of oil obtained varies from 2·5 to 5 per cent. *Juniperus virginiana* occurs over a very wide area in America, and some of the finest oil is obtained from the Florida cedar. This oil is one of those which is indispensable in certain classes of perfumery, especially in fine soap-making, where intensely "sweet" odours are not required. The wood in fine powder finds its way into much of the incense and similar preparations used either for ceremonial or fumigating purposes.

The oil is usually of a brownish colour, but it can be obtained almost water white, and although we know nothing definitely of what change occurs, it is certainly amongst those oils which improve in quality by keeping.

Pure cedar-wood oil has a specific gravity of from ·940 to ·960, and is always laevo-rotary. The limits, however, are wide, the oil varying from $-25°$ to $-40°$. According to Schimmel, 80 per cent. distils at between 125° and 155° at a pressure of 14 mm. The refractive index is very high, usually exceeding 1·5, and often rising to 1·51. The known

constituents of the oil are the sesquiterpene cedrene, $C_{15}H_{24}$, and the oxygenated body cedar camphor, or cedrol $C_{15}H_{26}O$. The former body has already been referred to. The latter, when pure, is a silky crystalline mass, with pleasant aromatic odour, melting at about 78° to 80°. It is suggested by Schimmel that cedrol is not a normal constituent of fresh wood, but is formed in it by keeping it under favourable conditions. This supposition has not, however, been experimentally justified except in so far as very old wood yields a semi-solid oil, which deposits much cedrol on cooling. At all events, only a small quantity occurs in normal oils, as is shown by the low acetylation figure. If the oil be acted upon by acetic anhydride, and the resulting product saponified, no more than from 6 to 8 per cent. of cedrol will be indicated. It must be remembered, however, that dehydration takes place to a small extent with acetic anhydride, so that the result is somewhat underestimated. Ten per cent. may be regarded as the maximum usually occurring in good oils. The figures found by the author for four pure samples (percentage of KOH to saponify the acetylated oils) are as follows: 2·32, 2·21, 2·13, 1·72.

For further details of the chemistry of the oil reference should be made to a paper by Rousett (*Bull. de la Soc. Chem.*, 1897, p. 485). In some of the American pencil factories an inferior oil is obtained by condensing the vapours obtained from the drying chambers, but this oil is of very indifferent odour and not much used.

Oil of Jamaica cedar or Honduras cedar is distilled from the wood of *Cedrela odorata*, a West Indian plant of an entirely different family. This oil is more correctly termed cedrela-wood oil, and will be referred to later. Other cedar oils, which have a right to the name, are the following. From *Cedrus Libani*, the enormous tree found in Lebanon and Taurus, and now a favourite in English grounds; this

is a brown oil of specific gravity about ·980 and laevo-rotary − 10° to − 20°. From *Juniperus Bermudiana;* this is a light-coloured and pleasant-smelling oil.

Corinto cedar-wood oil has a specific gravity of about ·906 and is laevo-rotary. Its botanical origin is uncertain. A Cuban oil, also of uncertain origin, is dextro-rotary, and contains cadinene, and a La Plata oil is optically inactive. An oil from Punta-Arenas is slightly laevo-rotary, of low specific gravity, and contains cadinene. These oils, of uncertain botanical origin, however, are of little commercial importance.

Pure cedar oil is fairly cheap, varying in price (as obtainable from wholesale druggists) from 1s. 9d. to 4s., or thereabouts, per lb., according to quality. Hence it is not much adulterated. It is employed, however, to adulterate other oils, notably santal-wood oil, and formerly also patchouli oil.

Oil of Turpentine.—Numerous members of the family of the *Coniferae* contain large quantities of resin, and oil consisting almost entirely of terpenes, in well-characterised resin ducts in the wood. This is especially the case with the various species of pine. The exudation from the wood, an oleo-resin, is often known as crude turpentine. Oil of turpentine, or, as it is generally called, turpentine or "turps," is the oil obtained by distilling this, leaving the crude resin or "rosin" behind. Before mentioning the chief varieties of turpentine, it will be convenient to briefly describe the process by which it is obtained, for example, in the United States. Here the principal source of the oil is *Pinus Australis*, usually known locally as the yellow or Georgia pine. During the autumn and winter months the trees are "boxed". This operation consists in making excavations of characteristic shape into the trunks of the trees, about six to eight inches above the roots. These excavations or "boxes" are made

so as to hold from one-half to one gallon, and in a day or two after they have been made, the trees are barked to the height of about three feet above the box, and some of the wood is also scraped off and hacks are made in the wood to allow the crude oleoresin to exude into the boxes. This exudation commences about March, and runs to the end of August, and, somewhat more slowly, during the next month or two. The crude turpentine is then baled out into rough barrels. As a rule, the trees are hardly worth treating for more than five or six years, as the oleoresin then yields little oil. Occasionally great exceptions to this rule are found. The crude turpentine is transferred to stills and subjected to a temperature of about 140° C., until the little water and volatile impurities present are driven off. Water is then added to the still, and the turpentine oil is distilled and separated from the watery layer. It is transferred to oak barrels holding about three hundredweight, in which packages it is exported. These barrels are very well made, and when empty are always worth about four shillings. Turpentine is a colourless liquid when pure, but easily resinifies and darkens on exposure to the air. It has a somewhat unpleasant odour, and is not used for perfumery purposes at all, but it finds very extensive employment as a solvent, and vehicle in the manufacture of varnishes and paints. It is also used for the manufacture of medicinal terebene, and, to a certain extent, for other pharmaceutical and medicinal purposes.

The following are the best-known varieties of oil of turpentine:—

American Turpentine.—This is chiefly obtained from *Pinus Australis*, but also to a certain extent from *Pinus taeda*, the loblolly pine. It is a colourless limpid liquid of specific gravity ·855 to ·870. It is almost invariably dextrorotary, to the extent of about + 10° to + 15°, but is rarely

slightly laevo-rotary. It commences to boil at 156° to 157°, and in good samples 88 to 99 per cent. will distil below 165°. Its chief constituent is pinene $C_{10}H_{16}$, and a little dipentene is also present.

French Oil of Turpentine.—This variety is chiefly obtained from the oleoresin of *Pinus pinaster*. Here again the chief constituent is the terpene pinene, and the great difference between this and American turpentine lies in the fact that the former is laevo-rotary, about − 18° to − 40°.

German Oil of Turpentine is chiefly the product of *Pinus sylvestris*, but *Pinus abies*, *Pinus vulgaris* and *Pinus picea* also contribute to it. Its specific gravity is ·860 to ·870, and it is dextro-rotary, about + 15° to + 20°. It contains pinene and sylvestrene.

Russian and Swedish Oil of Turpentine.—This variety is almost entirely obtained from *Pinus sylvestris* and *Pinus ledebourdii*. In general properties it resembles German oil, but it is rather more variable in specific gravity, etc. According to Tilden, it contains as much as 60 to 70 per cent. of sylvestrene. Its specific gravity is usually about ·870 to ·875, and its boiling point about 170°. It is dextro-rotary to the extent of + 20°. Of all the commercial turpentines it is of the least technical importance. It often possesses a disagreeable empyreumatic odour, due to the presence of the products of destructive distillation of the pine-wood.

Other less important turpentines are Hungarian (from *Pinus pumilio*); Austrian (from *Pinus laricio*); Carpathian (from *Pinus cembra*), and Finnish (similar to German). In addition, Venetian turpentine and Canada balsam yield oils. These latter, however, have practically no commercial interest.

The terebene of pharmacy consists of optically inactive terpenes, the result of the action of sulphuric acid on turpentine, which causes a certain amount of isomerisation, and

also changes the active terpenes into their inactive variety. For the manufacture of this, it is preferable to employ rectified oil of turpentine. Indeed for pharmaceutical purposes in general, it is usual to employ turpentine purified by redistillation.

Turpentine is sometimes adulterated with petroleum and with rosin spirit, and, rarely, with volatile portions of shale oil and coal tar. It is itself used very largely to adulterate other essential oils, both on account of its price and because it so closely resembles many other oils in chemical constitution.

The accompanying table (p. 104) is given by Allen (*Commercial Organic Analysis*), embracing certain properties of these bodies.

The chief points of importance to be noted in the examination of the oil are the specific gravity, boiling point and temperature of distillation, optical activity, and flashing point.

Good commercial turpentine has a specific gravity of ·858 to ·870, only occasionally passing these limits slightly. Russian oil has a higher gravity—often reaching ·875. The optical activity, as stated above, varies with the source, and this factor is only of value when studied in conjunction with the other features of the oil. The boiling point is usually 155° to 156°, and a considerable portion distils at below 160°. In the best class of oils at least 85 per cent. distils below 165°, often several degrees below this temperature. Russian oil, on the other hand, distils chiefly between 170° and 180°. When adulterated, the temperature of distillation rises gradually, and no large fractions are obtained at any definite temperature when the adulteration is at all excessive. The presence of ordinary petroleum spirit lowers the flash point of turpentine. When pure, it flashes at 92° to 95° F. when tested in Abel's flash point apparatus. With only 1 per

	Turpentine Oil.	Rosin Spirit.	Petroleum Naphtha.	Shale Naphtha.	Coal-tar Solvent Naphtha.
1. Optical activity	active	usually none	none	none	none
2. Specific gravity	·860-·872	·856-·880	·700-·740	·700-·750	·860-·875
3. Temperature of distillation	156°-180°	gradual rise	gradual rise	gradual rise	gradual rise
4. Action in the cold on coal-tar pitch	readily dissolves	readily dissolves	very slight action	very slight action	readily dissolves
5. Behaviour with absolute phenol at 20°	homogeneous mixture	homogeneous mixture	*no* apparent solution	homogeneous mixture, crystallises on cooling	homogeneous mixture
6. Behaviour on agitating 3 vols. with 1 vol. castor oil	*homogeneous* mixture	homogeneous mixture	two layers of nearly equal volume	like petroleum naphtha	—
7. Bromine absorption (dry)	203-236	184-203	10-20	60-80	—
8. Behaviour with H_2SO_4	almost entirely polymerised	polymerised	very little action	considerable action	moderate action

cent. of ordinary petroleum spirit this temperature is reduced by 10°.

According to Armstrong, a good indication of the presence of the usual adulterants is obtained by distillation with steam. A current of steam is allowed to pass into a definite volume of the turpentine contained in a flask attached to a condenser. Unless it has been allowed free access to the air for some time, the genuine oil leaves only traces of non-volatile matter, but old samples may leave up to 2 per cent. Usually, however, the presence of more than ·5 per cent. after steam distillation indicates the presence of unvolatilised petroleum oil. This is easily recognised by its low specific gravity and its fluorescence when dissolved in ether. If the residue consists of resin oil, it will form a bulky soap when rubbed with slaked lime. The specific gravity of the fractions coming over with the steam will largely assist in determining the presence of volatile adulterants.

For the approximate estimation of the amount of petroleum naphtha in adulterated turpentine, Armstrong recommends the following process: 500 c.c. of the sample is placed in a separator and treated with about 150 c.c. of sulphuric acid (two volumes of acid to one of water). The mixture is cautiously agitated, and if much rise of temperature is observed, the separator must be placed in cold water for a short time. The turpentine is gradually converted into a viscid oil, and when this has taken place, and no more heat is developed on repeated agitation, the acid is tapped off. The oily layer is then transferred to a flask and subjected to steam distillation. When all that is volatile with steam has passed over, the oily portion of the distillate is separated from the aqueous layer, and heated with half its volume of sulphuric acid previously diluted with one-fourth of its measure of water. The mixture is well agitated, the acid liquid separated, and the oily layer again distilled with steam.

When genuine turpentine is operated upon, the volatile portion of this second treatment consists merely of cymene and a small quantity of paraffinoid hydrocarbons. It never exceeds 4 to 5 per cent. of the volume of the original sample, and with care is as low as 3 per cent. If the volume notably exceeds 5 per cent., it is advisable as a precaution to repeat the treatment with the (4 to 1) acid. When treated in this manner, petroleum naphtha is not appreciably affected, hence the proportion may be fairly estimated by making an allowance of 4 to 5 per cent. from the volume of volatile oil which has survived the repeated treatment with sulphuric acid. A further purification may be effected by violently agitating the surviving oil with several times its volume of concentrated sulphuric acid heated to 50° or 60°. This treatment can be repeated if necessary, after which the residual hydrocarbon is separated, steam distilled, and again measured, when the surviving oil from pure turpentine oil will not exceed from one-half to one per cent. of the original sample. Any excess over this will be the minimum quantity of petroleum naptha present. Shale naptha cannot be at all estimated in this way. The behaviour of the oil on distillation is the best indication of the presence of rosin spirit, as the temperature rises gradually, and no considerable fraction is obtained at 158° to 160° if much rosin spirit be present.

The *British Pharmacopœia* (1898), in which turpentine is official, requires it to be soluble in an equal volume of glacial acetic acid, and to boil between 160° and 180°.

Juniper-wood Oil.—It is said that a volatile oil is obtained by distilling the wood of *Juniperus communis* with steam, but commercial juniper-wood oil is merely turpentine distilled over juniper-wood, or more usually a mixture of juniper berry oil and turpentine. So-called juniper-wood oil, however, finds a certain amount of employment as a cheap substitute for the oil of juniper berries. By the distinctive distillation

of the wood of *Juniperus oxycedrus*, an empyreumatic oil known as oil of cade (*Oleum cadinum; huile de cade*) is obtained. This is a dark-brown tarry liquid of empyreumatic odour, employed in the treatment of certain skin diseases. Its principal constituent is cadinene, but as it is not one of the essential oils proper it need not be further discussed here.

II. Fruit Oils.

The most important oils obtained from the fruit of coniferous trees are juniper (from berries of *Juniperus communis*), and fir cone oil (from cones of *Abies pectinata*).

Juniper Berry Oil.—The plant yielding this oil is *Juniperus communis*, a native of Greece, and widely distributed over Europe. It is a small shrub or tree varying from two to six feet in height, but in parts of Norway it forms a forest tree some thirty to forty feet in height. The Italian berries, however, are most valued for oil. According to Pereira, the juniper of the Bible was a leguminous plant, probably the broom or furze tree. Fraas considers the κέδρος μικρα of Dioscorides was our juniper. The plant is usually diœcious, and the scales of the cones, when ripe, become succulent, and cohere to form a kind of berry (galbulus). These berries are rich in sugar, and by their fermentation and distillation the well-known beverage, gin, is obtained, which owes its characteristic flavour to the oil of juniper. The *British Pharmacopœia* states that the oil is distilled from the full-grown unripe fruit. But with reference to this point, Schimmel (*Report*, October, 1898, p. 30) states that "this is an error, at least no such oil is distilled on a large scale. It is an antiquated idea, originating with Zeller, that unripe fruits render a larger yield in oil than ripe ones. In any case, the oil distilled from unripe berries in all essential qualities is inferior to normal oil of ripe fruits." The following are

given by Schimmel as the average yields of oil from plants grown in certain districts:—

Bavarian .	1·2 per cent.	Italian .	1 to 1·5 per cent.
East Prussian	·6 per cent.	Polish . .	·9 per cent.
Thuringian .	·7 per cent.	Hungarian	·8 to 1 per cent.
Swedish .	·5 per cent.		

The only constituents of oil of juniper which have been ascertained with certainty are (1) the terpene, pinene $C_{10}H_{16}$; (2) the sesquiterpene, cadinene $C_{15}H_{24}$; (3) juniper camphor, a crystalline body probably belonging to the series of terpene alcohols. According to Schimmel, the chief, if not only, constituent of the stearoptene is a sesquiterpene alcohol melting at 165° to 166°; (4) an ester boiling at about 180°, probably the acetic ester of the above-mentioned alcohol.

The *British Pharmacopœia* demands that the specific gravity of the oil should lie between ·865 and ·890, and that it should be soluble in 4 volumes of 95 per cent. alcohol. The age of the berries from which the oil is distilled produces a marked effect on the specific gravity of the oil, as does also the time for which the latter has been kept, as exposure to the air causes gradual resinification. The solubility also decreases when the oil is kept. Rectification also naturally alters the specific gravity, which depends chiefly on the relative proportions of terpene (sp. gr. = ·860), and sesquiterpene (sp. gr. = ·920). The limits ·865 and ·890 are certainly those which should be accepted for genuine, good oils. The approximate proportions of pinene and cadinene may be judged by a fractional distillation, as pinene boils at 156° and cadinene at 274°. The results vary largely according to the fractionating apparatus used, but with a series of bulbs, from 25 to 35 per cent. is obtained between 155° and 160°, and from 10 to 20 per cent. between 270° and 280°. The oil is always laevo-rotary, never exceeding − 10°, usually, in the author's experience, from − 4° to − 6°. With

our present knowledge of this oil, no further analytical methods are yet available.

Juniper oil is of considerable commercial importance. It is employed largely in the manufacture of artificial gin, which is a spirituous solution which is not obtained by the fermentation of the berries. Indeed, essence of gin, which is chiefly, if not entirely a solution of the oil in alcohol, is a regular commercial article. The oil is also employed in medicine, as a sudorific and diuretic. The berries are imported from various European ports, in bags and barrels, but the Italian berries are preferred to all others. The importation in bags is becoming less common, as the berries are very liable to be bruised, when fermentation may set in.

The oil from the berries of *Juniperus phoenicea*, from Smyrna, has been examined by Schimmel. The berries, which are bright red, yielded 1 per cent. of oil of specific gravity ·859 and optical rotation − 4°55′. The berries of *Juniperus oxycedrus* (Dalmatian) yield an oil of specific gravity ·851 and optical rotation − 8°.

Fir Cone Oil.—This oil, obtained from the young cones of *Abies pectinata* (*Abies excelsa*), is sometimes sold under the name of pine oil. It contains very little bornyl acetate (the ester characteristic of the fine pine needle oils), never more than 2 per cent., but consists almost entirely of *laevo*-pinene and *laevo*-limonene. Its specific gravity is about ·855 to ·865, and it is laevo-rotary up to − 70°.

III. Leaf Oils.

Thuja Oil.—This oil is obtained by distillation with steam of the leaves and possibly also the small twigs of *Thuja occidentalis*, the well-known *arbor vitæ*, sometimes also called the white cedar. The yield of oil is from ·5 to 1 per cent. It is almost colourless, but by oxidation becomes slightly greenish or yellow. Its odour is not particularly

pleasant, somewhat recalling that of tansy oil. It is frequently adulterated with cedar oil, pine-leaf oils or turpentine, but when pure has a specific gravity of not less than ·910, usually from ·915 to ·925. Its optical activity is given by Schimmel as − 6° to − 13°, but the author has found genuine oil with a little higher rotation than this, so that − 6° to − 14° may be regarded as outside limits. The earliest scientific investigation of this oil is that of Jahns, but that of Wallach, undertaken when our knowledge of the group of compounds contained in the oil was a little more advanced, is now the standard work. The chief constituents of the oil are pinene, *laevo*-fenchone $C_{10}H_{16}O$, and the isomeric ketone, thujone, which also occurs in the oils of tansy, wormwood and sage. Traces of esters, probably of acetic and formic acid, are also present, and possibly carvone. The highest boiling constituents of the oil have not yet been thoroughly examined, but Wallach believes them to contain the last-named body in the inactive form. A pure oil should have the characteristics mentioned above, *viz.*, specific gravity ·910 to ·925; optical activity − 6° to − 14°; and should be soluble in three times its volume of 70 per cent. alcohol. Thuja oil is not of much commercial importance.

An oil has been obtained from the roots of *Thuja orientalis* with a specific gravity ·979, but little is known of its composition.

Oil of Savin is obtained from the fresh twigs of *Juniperus sabina*. It is an oil which finds but a limited employment in legitimate pharmacy as a uterine stimulant and emmenogogue. It is of no value for perfumery purposes, as its odour is somewhat unpleasant. It is occasionally used for criminal purposes, and one case is recorded of a medical man being sentenced to transportation for having used it with the intention of procuring abortion (*vide*

Medical Times and *Gazette*, 17th April, 1852, p. 404). It was official in the 1885 *British Pharmacopœia*, but it has been wisely omitted from the 1898 edition. The yield of oil from the twigs is fairly high, varying from 3 to 5 per cent., and the oil only fetches a few shillings a pound, unless it is English distilled, when it is worth nearly as much per ounce as the foreign oil is per pound.

The oil contains a number of constituents, of which Wallach first characterised the sesquiterpene, cadinene. A considerable proportion of terpenes are present, which appear to consist chiefly of pinene. The most recent work on the subject, however, is that of Fromm (*Berichte*, 1898, p. 2025), who separated the oil into three main portions by fractional distillation. The earliest distillate, below 195°, consisted mainly of terpenes, the middle portion, 195° to 235°, consisted chiefly of ethereal salts, and the last portion, 235° to 310°, consisted of cadinene and some resinous bodies, which were possibly the effects of heat on the terpenes. The middle fraction yielded an oil boiling at 222° to 224°, which was shown to be the acetate of an alcohol $C_{10}H_{15}OH$, which the author terms sabinol (Schimmels had previously identified an alcoholic acetate, but they considered the formula of the alcohol to be $C_{10}H_{17}OH$). The alcohol, obtained by hydrolysing the acetate, is a colourless oil, boiling at 208° to 209°, and with only a faint odour. According to Schimmel (*Report*, October, 1895, p. 44), the amount of this ester present is about 40 per cent., and there is in addition about 10 per cent. of the free alcohol in the oil.

A pure oil, free from turpentine, which is often used to adulterate the French oil, should have a specific gravity of ·910 to ·928, and should be dextro-rotary + 40° to + 60°. It should be soluble in its own volume of 90 per cent. alcohol, and should not yield more than 25 to 28 per cent. of distillate below 200°. When a sufficient number of samples have been

examined, it may be possible to fix an ester and alcohol limit, but at present it would be unwise to do so.

Cedar-leaf Oil.—The true cedar-leaf oil may be regarded as the distillate of the leaves of *Juniperus virginiana*, the red cedar, but the confusion implied in the name "cedar" is reflected in the enormous variations met with in commercial samples of so-called cedar-leaf oils. No doubt the leaves of *Thuja occidentalis* and *Chamæcyparis sphæroidea* contribute largely to the commercial oil. Brannt, indeed, describes the oil as having a "penetrating, disagreeable odour," and as "therefore not suitable for perfumery purposes". As a matter of fact, the pure oil has a pleasant, sweet odour, and possesses a specific gravity ·883 to ·888. Its optical rotation varies from + 55° to + 65° (according to Schimmel, + 59° 25′). The examination of a pure sample by Schimmel showed that it contains limonene, cadinene, borneol and bornyl esters, probably including bornyl valerianate; other terpenes are also present.

The true *Juniperus virginiana* leaf oil is more expensive than the corresponding oil from cedar-wood—being worth from three to five times as much, in fact, and as the oils from thuja and other leaves are also less costly, it is a matter of importance that the oil should be carefully examined. Six commercial samples and one pure sample, examined by Schimmel & Co., gave the following results:—

	Sp. gravity.	*Optical rotation.*	*Solubility in 70 °/₀ alcohol.*
Pure oil	·887	+ 59° 25′	very insoluble.
1 . .	·897	− 12° 25′	insoluble.
2 . .	·886	− 3° 40′	insoluble.
3 . .	·887	− 24° 10′	insoluble.
4 . .	·920	− 10° 25′	soluble in 4 parts.
5 . .	·918	− 10° 55′	soluble in 5 parts.
6 . .	·905	− 10°	insoluble.

Sequoia Oil is obtained from the leaves of *Sequoia gigantea*, the Californian mammoth tree. Lunge and Steinkauler obtained the oil from smaller ornamental trees

grown in Zurich. The first portion of the distillate contained a crystalline hydrocarbon $C_{13}H_{10}$, melting at 105°, which these chemists termed sesquoiene. The later distillate contained a dextro-rotary terpene and an oxygenated body $C_{10}H_{20}O_3$. These bodies require further investigation, but as the oil has no commercial importance, it has not attracted much attention so far.

Pine-needle Oil.—There are few oils in commerce in regard to which so much confusion exists as in the case of the so-called pine-needle oil. The oils from the leaves of the *Coniferæ* consist so largely of terpenes that much of the cheap commercial oil consists largely of turpentine, either mixed with a little of the genuine oils, or distilled over pine leaves. We are indebted chiefly to Bertram and Walbaum for a careful investigation of the properties of pure oils of known botanical source. Of these, the following are the most important, known as pine-needle oils. The oil of *Abies pectinata* (*A. excelsa*), distilled from the needles and young shoots of this pine (the Norwegian spruce fir), is perhaps the most valued of all the pine-needle oils. It possesses a fine fragrant odour, and is exceedingly useful for fine perfumery where the best pine odour is required. It has been found to contain *laevo*-pinene, *laevo*-limonene, a sesquiterpene (possibly cadinene) and *laevo*-bornyl acetate. The latter ester, which is characteristic of the pine odour, occurs to the extent of 4·5 to 7·5 per cent. It is a colourless oil, of specific gravity about ·865 to ·875 and laevo-rotary, according to Schimmel, from − 20° to − 60°. The oil from the young cones of this tree is often sold as pine-needle oil, but it differs from the above-described in containing very little bornyl acetate (*vide supra*).

The oil of *Pinus sylvestris*, the true Scotch fir, was official in the *British Pharmacopœia* in 1885, but has been replaced in the new edition by that of *Pinus pumilio*. The former

oil (*P. sylvestris*), distilled from Swedish leaves, and examined by Bertram and Walbaum, had a specific gravity ·872, and was dextro-rotary + 10° 40′. The constituents found were *dextro*-pinene, *dextro*-sylvestrene and bornyl acetate (3·5 per cent.). A fractional distillation showed that 44 per cent. distilled between 160° and 170°, and 40 per cent. between 170° and 185°. A sample distilled by themselves from German-grown trees was also examined by these chemists, and had a specific gravity ·886 and an optical rotation of + 10°; 10 per cent. distilled between 160° and 170°, and 46 per cent. between 170° and 185°. *Dextro*-pinene, *dextro*-sylvestrene, cadinene and probably dipentene and bornyl acetate were found in the oil. Umney has examined a sample distilled by himself from leaves gathered near Sevenoaks, and found it to possess a specific gravity ·8855, and, in contradistinction to Bertram and Walbaum's oil, it was *laevo*-rotary − 19°. About 3·5 per cent. of bornyl acetate was found, and Umney concludes that not more than 15 per cent. should distil below 170°. Taking as criteria the two oils which were actually distilled by these chemists, one may infer that the pure oil from this source should possess a specific gravity of not less than ·880; should not rotate the plane of polarisation more than 20° either to the right or the left (Schimmel has, however, found an American oil, probably genuine, as high as − 25°), and should not yield a distillate below 170° of more than 15 per cent., nor one between 170° and 185° of less than 40 per cent. It may be noted that the 1885 *Pharmacopœia* allowed so low a gravity as ·870°. In order to determine how far the difference in rotary power observed by Bertram and himself could be accounted for by the season at which the leaves were gathered, Umney distilled samples at different times of the year, and, although he found that oil distilled in December was laevo-rotary to the extent of − 7° 45′ as against − 19° for oil distilled in June, he concludes that soil and climate are the chief factors which

determine the difference in rotary power. True oil of *Pinus sylvestris* is not an article of commerce. The commercial oil is the distillate of various other pines.

The oil of *Pinus pumilio* contains *laevo*-pinene, *laevo*-phellandrene, sylvestrene, cadinene, dipentene and bornyl acetate (4 to 7 per cent.). This oil has a specific gravity of ·865 to ·875, and is laevo-rotary to the extent of − 5° to − 10°. A sample fractionated by Umney gave only 2 per cent. below 165°, and as much as 59 per cent. between 165° and 180°. This oil is official in the present edition of the *British Pharmacopœia*, which demands that its specific gravity should fall between ·865 and ·870, and its optical rotation between − 5° and − 10°. Not more than 10 per cent. is to distil below 165°.

The oil from the needles of *Abies sibirica* is one of the cheapest of the genuine pine-needle oils, and is not held in much favour. Its specific gravity is ·910 to ·920, and it is *laevo*-rotary − 40° to − 45°. It contains a small percentage of bornyl acetate.

Picea vulgaris needles yield a small amount of an oil of specific gravity ·880 to ·890, laevo-rotary about − 20°, containing *laevo*-pinene, *laevo*-phellandrene, dipentene, cadinene and *laevo*-bornyl acetate. The oil from *Pinus picea* is very similar to this, usually having a specific gravity ·872 to ·876 and an optical rotation of about − 50°. *Abies canadensis* yields the so-called spruce or hemlock spruce oil. This has a specific gravity of about ·905, is *laevo*-rotary about − 20°, and contains *laevo*-pinene, cadinene and *laevo*-bornyl acetate (3·6 per cent.), and also a small amount of camphene.

The oil from *Pinus nigra* is characterised by its containing 50 per cent. of bornyl acetate. Its specific gravity is about ·925 and its rotation − 40°. It was examined by Kremers. A number of other pine-needle oils have been examined, but

it is not necessary to devote further space to them; their characteristics are given in the appended table (p. 117).

From a commercial aspect these various pine-needle oils have remarkably different values. There seems but little doubt that the greater part of the *genuine* pine-needle oil of commerce sold as oil of *Pinus sylvestris* is distilled from *Abies pectinata* (*A. excelsa*)—in the author's experience chiefly from the young cones; the true oil of *Pinus sylvestris* is rarely met with. That from *Pinus pumilio* is of course a regular commercial article, as are also certain others which can be obtained correctly labelled, such, for example, as the oil of *Pinus sibirica*. In addition to the difficulties arising from this confusion in the names, gross adulteration with turpentine is regularly met with. The ester to which the oil owes the character of its odour, bornyl acetate, can be obtained on the market, but it has not ousted the natural oils from the position they hold both as perfumes and drugs. For certain throat affections they find regular employment either as inhalations or taken internally in the ordinary way. Taken from a current price list, the value of some of the market oils, as compared with that of bornyl acetate, is as follows. Per lb: *Abies excelsa*, 11s. 2d.; *Pinus pumilio*, 7s. 2d.; *Pinus sibirica*, 2s. 6d.; and bornyl acetate, 38s.

Cypress-leaf Oil.—The leaves of *Cupressus sempervirens* yield about 1 per cent. of an oil of specific gravity ·885, and optical rotation + 5°, consisting largely of terpenes. It is a somewhat expensive oil, said to be very useful as a remedy for whooping cough when inhaled.

TABLE OF PINE OILS (AFTER SCHIMMEL).

Oil.	Sp. Gr.	Rotation.	Constituents.
Abies excelsa (leaves)	·865-·875	- 20° to - 60°	Pinene, limonene, *cadinene*, bornyl **acetate** (4 to 7 per cent.).
„ „ (*young cones*)	·855-·870	- 60° to - 80°	Pinene, limonene, bornyl acetate (·5 to 1 per cent.).
Pinus sylvestris	·880-·885	+ 20° to - 20°	Pinene, sylvestrene, dipentene, cadinene and bornyl acetate (3·5 per cent.).
„ **pumilio**	·865-·875	- 5° to - 10°	Pinene, phellandrene, sylvestrene, cadinene, bornyl acetate (4 to 7 per cent.).
Abies sibirica	·910-·920	- 40° to - 45°	Bornyl acetate.
Picea vulgaris	·888	- 21° 40′	Pinene, phellandrene, dipentene, cadinene, bornyl acetate.
Pinus nigra	·925	- 39° 40′	Bornyl acetate (50 per cent.).
„ **palustris**	·861	+ 23° 55′	
„ **cubensis**	·868	+ 9° 6′	
Abies balsamea	·892	- 29° 1′	Pinene (?), bornyl acetate.
„ **canadensis**	·907	- 20° to - 26°	Pinene, *camphene, cadinene*, bornyl acetate.
Picea nigra	·913	- 23° 50′	Bornyl acetate (38 per cent.).

OILS OF THE ANGIOSPERMS.—I. MONOCOTYLEDONS.

N. O. Gramineæ.

The essential oils of this natural order are obtained almost entirely from the *Andropogon* family. Those of which anything reliable is known are citronella, lemon-grass, palmarosa (Indian geranium), veti-vert, and one or two others of doubtful origin; these are commercial products of the highest importance, as they are used on an enormous scale either for direct perfumery, or for the preparation of perfumes of an entirely different nature, by chemical methods. For many years the exact botanical sources of these oils was a matter of doubt, but, in the case of the more important oils, at all events, these may now be regarded as settled.

Citronella Oil.—This oil is distilled from the "Indian grass," *Andropogon nardus*, chiefly in Ceylon. It is a pale yellow oil of very powerful odour, on which account, together with its low price (varying on the market from about 1s. to 1s. 6d. per lb. lately), it is more extensively employed in cheap soap perfumery than any other essential oil. The chemistry of the oil was first seriously attacked by Dodge (*American Journal of Chemistry*, xi., p. 456), who showed that it contained a large quantity of the aldehyde citronellal. Other workers have since shown that it contains, in addition, the terpenes camphene and dipentene, the alcohol geraniol, and small quantities of borneol and methyl-heptenone. Possibly linalol, methyl-eugenol and a sesquiterpene also exist, but the presence of these requires confirmation.

The oil found on the market is frequently adulterated with kerosene, and occasionally with an oil whose identity is not yet settled, but which appears to be somewhat similar in properties to the oil of gurjun balsam.

The specific gravity of the pure oil is very variable, and while it is not possible to define the limits closely, it may be taken that anything outside ·885 to ·920 is impure. The optical rotation, which is laevo-rotary, varies with the specific gravity, the oils with a high gravity being more highly rotary than those with a lower gravity. The only other criteria of the purity of the oil are its solubility in alcohol and its acetyl number. One volume of oil should yield a clear, or at most, slightly opalescent solution with 2 to 3 volumes of 80 per cent. alcohol at 20°, and no oily drops should separate even when 10 volumes of the alcohol are added. It is important that the clearness of the solution of the oil in 3 volumes of the alcohol should not be impaired by the addition of more alcohol, as although kerosene will render it partially insoluble in the smaller quantity of alcohol, an adulterant has been noticed which only rendered the solution turbid when more of the 80 per cent. alcohol was added. The nature of this has not been determined (*vide supra*).

The acetylation method, so far, appears to be of somewhat doubtful value. Although sometimes spoken of as the estimation of geraniol, this is incorrect; for citronellal is easily converted into isopulegol acetate by acetic anhydride, with the result that, although the determination may be calculated as geraniol, it actually includes the citronellal as well. A perfectly empirical and meaningless result is thus obtained. This is emphasised by the following figures quoted by Schimmel & Co. for fourteen samples, which they are convinced were pure (*Report*, Oct., 1898).

	Rotation.	*Sp. gravity.*	*Geraniol.* Per cent.
1	− 0° 46′	·892	88·6
2	− 0° 54′	·892	80·9
3	− 0° 48′	·892	82·5
4	− 1° 18′	·890	85·4
5	− 1° 32′	·886	85·1

	Rotation.	Sp. gravity.	Geraniol. Per cent.
6	− 2° 20′	·888	83·4
7	− 1° 25′	·894	81·8
8	− 0° 53′	·890	90·6
9	− 7° 10′	·919	56·9
10	− 0° 34′	·888	86·4
11	− 9° 53′	·915	65·5
12	− 20° 37′	·896	50·4
13	− 7° 13′	·918	54·1
14	− 9° 36′	·908	61·1

Umney and Swinton (*Year Book of Pharmacy*, 1897, p. 365) have endeavoured to explain the differences in the commercial oils of apparently genuine character. They have come to the conclusion, chiefly by means of experimental distillation of the oils with steam, that the high gravity oils are the native distilled oils over an open fire, whilst the lower gravity oils are steam distilled, and that the differences do not at all depend on any variation in the grass used. The high specific gravity is regarded as being due to a hitherto undescribed sesquiterpene, and the high optical rotation to a highly active terpene.

Schimmel, on the other hand, states that there are two different kinds of citronella grass distilled in Ceylon, but whether they are true varieties, or whether one is merely a degeneration, is not yet known. Under any circumstances, it is certain that the high gravity oils are of poorer odour, containing much less aldehyde and alcohol, to which the oil chiefly owes its value.

The aldehyde citronellal, possessing the characteristic odour of the oil, is also a commercial product. It is, however, from fifteen to twenty times as expensive as the oil itself, and certainly does not possess any commensurate advantages. The purest commercial samples examined by the author were slightly optically active, perfectly colourless liquids, of specific gravity about ·873.

The grass is cultivated almost entirely in the south of

Ceylon. According to Fritzsche, somewhere between 40,000 and 50,000 acres are devoted to it, and but little attention is necessary. The growth is continuous, and three harvests can be obtained annually in very favourable years, but usually two are found sufficient—one in July or August and one in December, January or February. The yield of oil is about sixteen to twenty bottles (22 oz.) per acre for the summer crop, and five to ten for the winter crop. After a lapse of fifteen years the plants become exhausted, and new plants become necessary. There are somewhere about 600 stills at work on the island, and the enormous output of well over 1,000,000 lb. per annum shows to what an extent this oil is used. So powerful is its odour and so cheap is the oil that it is now frequently used not only for perfuming cheap toilet soap, but also to cover the disagreeable odour of common hard and soft soap. The distilleries are usually in a shed, and consist of a steam boiler with a safety valve and water indicator, resting upon a solid foundation, two cylindrical stills about 6 ft. to 7 ft. high, and 3 ft. to 4 ft. broad. These are connected with a spiral condenser in a tub of cold water, the oil eventually being collected in a receptacle underground, which can be locked in order to prevent the natives from stealing it. The accompanying diagram, reproduced from the *Chemist and Druggist*, illustrates the arrangement (p. 122).

A still 7 ft. high and 4½ ft. in diameter produces about 350 to 450 oz. per day. Most of them are as that illustrated, although there are some which are arranged for an open fire distillation.

Lemon-grass Oil.—This oil is the product of distillation of the grass *Andropogon citratus*, a native of the continent of India and of Ceylon. Cochin China, Ceylon and Singapore are the chief centres of cultivation, although the grass is found over a very wide tract of the Indian peninsula and in

the West Indies. The greater part is exported from the ports on the Malabar coast. With regard to its preparation, much that has been mentioned under citronella oil holds good here also, but, of course, the fact that the oil does not enjoy nearly so large a consumption as citronella oil accounts for its preparation being more in the hands of the natives than the last-named oil. The annual production of lemon-grass oil appears to be about 50,000 lb. Its chief use is for perfumery, in which it plays an important part, as it has an odour resembling the true verbena, and is often known as Indian

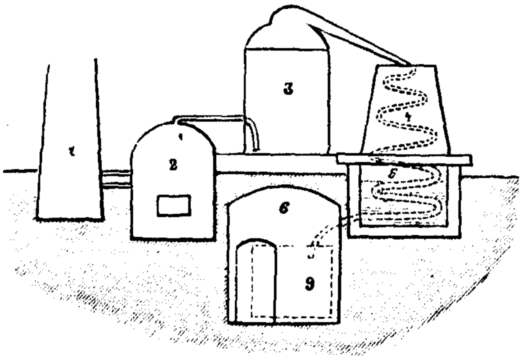


FIG. 13.—CITRONELLA OIL STILL.
1, chimney; 2, steam boiler; 3, still; 4 and 5, condenser; 6, underground cellar; 9, receiver.

verbena. With regard to price, it has been the subject of speculative dealings, hence it has varied from a few pence—1½d. even at one time—to about 1s. an ounce during the last few years. In addition to its extensive use in perfumery, it has lately found considerable employment for the preparation of citral, its chief constituent, for the manufacture of ionone. It is also used to some extent either as it is, or as citral, to adulterate oil of lemons. Attempts have been made, successful to an extent, but utterly misleading in their effects, to make the citral content the basis of the value of oil of lemons.

Hence the addition of small quantities of lemon-grass oil or citral to lemon oil. This will be again referred to under that oil.

Lemon-grass oil is a yellow to brownish oil, of specific gravity ·895 to ·905. It is often practically inactive optically, and should never vary more than from + 3° to - 3°. It is often adulterated with fixed oils, which not only alter its specific gravity, but also interfere with its solubility in alcohol. When pure, it dissolves to a clear solution in three times its volume of 70 per cent. alcohol. Its most important constituent is citral, which occurs in it to the extent of from 75 to 85 per cent. In addition to this, methyl-heptenone and geraniol traces of citronellol, and possibly linalol have been found. Terpenes occur to the extent of about 10 per cent. According to Stiehl, these consist of limonene and dipentene, and there is also a trace of cymene. These are the only constituents which can be said to be known to exist in the oil. The oil is chiefly dependent, if not entirely so, for its value on the percentage of citral it contains. Hence it is of importance to be able to estimate this constituent, at all events, with some degree of accuracy. This can be done by shaking the oil with solution of bisulphite of sodium, as described in a former chapter. It must be remembered, however, that this is only an approximate estimation, as a certain amount of the citral is converted into water soluble sulphonic acid derivatives, and a certain amount remains unabsorbed. For comparative purposes, however, it is exceedingly useful. The preparation of ionone (artificial violets) from lemon-grass oil direct, and from the separated constituent, citral, are subjects of patents. From this point of view it is important to know if citral is really the main constituent of the oil. If it were not so, the correctness of the patent specification would be open to attack, and the results might be of importance. According to most chemists who

have worked seriously on this oil, citral is the only aldehyde present in the oil, with the exception of traces of an isomeric aldehyde, and of citronellal. Upon this point Tiemann, Semmler and Doebner, the three chief authorities on this oil, are completely agreed. Quite recently Stiehl (*Jour. prakt. Chem.*, 1898, p. 51) has claimed to have separated the aldehydic constituent into three different bodies. He urges that the large amount of citral found in the oil usually, is due to the isomerisation of the other aldehydes by means of the bisulphite of sodium used in separating it, which is generally too acid. If this salt be perfectly pure he claims that this isomerisation does not take place. These aldehydes he terms citral (the aldehyde usually known as such), allolemonal and citriodoraldehyde, and he gives the following as their properties:—

	Citriodoraldehyde.	*Allolemonal.*	*Citral.*
Boiling point	228°-229°	233°-235°	225°-227°
Sp. gravity at 20°	·8883	·9017	·8868
Rotation	0°	− 5° 6′	0°
Melting point of compound with naphthocinchoninic acid	204°	235°	197°

Doebner, however, has shown—in the author's opinion conclusively—that these other aldehydes are merely impure citral, and that the former statements made regarding the oil are correct. Tiemann and Semmler have also repeated their former work and confirmed it in every respect (*see also under* "Citral," p. 136).

Indian Geranium Oil.—This oil is in no way related to true geranium oil, except on account of its similar odour. It occurs in European commerce under the names "Indian geranium oil," "Turkish geranium oil," "palmarosa oil," and "ginger-grass oil". Distinctions have often been made between these commercial products, and while it is possibly uncertain as to whether the botanical source of ginger-grass oil is absolutely identical with that of "Indian geranium

oil," it appears certain that the only differences existing between the others, are those of fineness of odour and freedom from adulteration. The oil is distilled in India from the grass *Andropogon Schœnanthus*, which grows wild in large tracts in the northern and eastern provinces, especially in the North-West and the Punjaub; it is also abundant in the Deccan, Central India and Kashmir. According to Schimmel, the most productive districts are Nagpore-Khandesh and Jubbulpore. The following account, from part vi. of *Pharmacographia Indica*, is particularly interesting: "The oil distillers in Khandesh call the grass *Motiya*, when the inflorescence is young and of a bluish-white colour; after it has ripened and become red, it is called *Sonfiya*. The oil obtained from it in the first condition has a more delicate odour than that obtained from the ripened grass. The *Motiya* oil is usually mixed with the second kind, which by itself would not fetch a good price in the European market. The grass grows freely, though not very widely, on open hillsides in West Khandesh, especially in Akráni. The original seat of the manufacture was Pimpalner, but as the oil is in great demand, the manufacture has of late spread to Nandurbár, Sháháda and Taloda. The makers are Mussulmen, who at the close of the rains, about September, when the grass is ripening, buy it from the Bhils, stack it and set stills at the sides of brooks where wood and water are plentiful. In 1879-1880 the number of stills was 197, producing about 71 cwt. of oil. More than 100 stills are worked in Nandurbár alone, and the increase of the manufacture is prevented only by the scarcity of the grass. The yield is about ·3 per cent. The oil is packed in skins and sent on bullock back over the Kundaibári Pass to Surat and by Dhulia and Manmad to Bombay." From Bombay it is exported to the Red Sea ports, Constantinople, Trieste and London.

The oil is a pale yellow liquid (often dark on account of the crude methods of distillation used by the natives, wherein too little water is used in the stills, with the result that the grass is burned), but frequently water white when rectified. It has a characteristic geranium odour, and is a most popular perfume where an odour recalling roses and geranium is required at a comparatively low price. At the time of writing, this oil is about 7s. 6d. to 10s. per lb. in small wholesale quantities, or about half the price of fine Algerian or Réunion geranium oil. When pure the oil has a specific gravity of from ·885 to ·896 and is almost inactive optically, rotating from $-2°$ to $+2°$, usually under 1° either way. The oil should dissolve in three times its volume of 70 per cent. alcohol. The ascertained constituents of the oil are the alcohol geraniol, esters of this alcohol (chiefly the acetic and caproic esters), methylheptenone (?) and the terpene dipentene. The odour value is entirely due to the geraniol and its esters, hence their estimation becomes of some importance. The esters do not require less than 3 nor more than 5 per cent. of potash for saponification. The usual amount of esters present is from 10 to 15 per cent. The free geraniol varies from 65 to 85 per cent. This is estimated in the usual way by acetylation —converting the geraniol into its acetic ester, and saponifying, as described in a previous chapter. The total geraniol (free and combined) varies from 75 to 92 per cent. Schimmel gives the following figures for four pure samples :—

GERANIOL.

Combined.	*Free.*	*Total.*
1. 12·1	76·36	88·46
2. 13·55	69·98	83·33
3. 8·67	68·23	76·9
4. 8·48	83·15	91·63

The oil is often adulterated, notably with fixed oils and

with turpentine or petroleum oil. All such adulterants are easily detected, as they greatly interfere with the solubility in alcohol, and, in the case of fatty oils, leave a non-volatile residue when steam distilled. When turpentine is added, the optical activity is totally altered and the ester and geraniol contents lowered.

The legitimate use of this oil is, of course, for perfumery, in which *rôle* it is handicapped by the finer odour of the true geranium oils. The difference in price, however, acts largely as a set-off in this respect. The active body geraniol is also a commercial product now, being prepared from various sources, notably from citronella oil. The rhodinol of commerce appears to be a mixture of geraniol and other alcohols, chiefly citronellol. Both of these bodies are, however, more expensive than the Indian geranium oil.

It also finds extensive use as an adulterant of either otto of roses, or of true geranium oil, the latter being also sometimes employed to adulterate otto of roses. An extraordinary use for this oil is suggested by Balfour in the *Cyclopædia of India*. He says that "grass oil has the property of preventing the loss of hair that occurs after some acute diseases: it is said to produce a new growth of hair". Whether this is true or not is uncertain.

Oil of Veti-vert.—This oil, also known as oil of vetiver or oil of cuscus, is the product of distillation of the root of *Andropogon muricatus*, Retz. (*A. squarrosus*, Linn.). These roots are known in Bengal under the name of khas-khas, from which the name cuscus is easily traced. The plant is a perennial tufted grass growing to a good height, and is found all over the country near the Coromandel coast, Mysore, Bengal, Burma and the Punjaub. It is also found in Réunion and Mauritius and in the West Indies. In contradistinction to the grasses above described, the leaves themselves are practically odourless, whilst the roots have

a strong, agreeable odour. On distillation, the first fractions passing over are much more volatile and lighter than those which come over with difficulty towards the end of the distillation. These "light" and "heavy" oils can be separated by using a steam-jacketed still with steam at a pressure of about 10 lb., until no more oil comes over. The heavy oil is then obtained by passing steam at a higher pressure direct into the retort. The oil distilled in Europe, however, is usually, if not always, a single distillate, and the fractionated oils are scarcely commercial articles. The so-called "light" oils appear to be merely adulterated veti-vert oil. The yield of oil is a matter of much disagreement. According to Piesse, 100 lb. of oil yield about 9 or 10 oz. of oil, whilst Watts states that only 2 oz. are obtained. Other observers give from ·2 to ·4 per cent. Probably about 1 per cent. is the usual average. Much of the oil (which is entirely used for high class perfumery) as found in commerce is adulterated, frequently with a fixed fatty oil. But little is known of the chemistry of its constituents, and only a comparatively few samples have been examined at all. The specific gravity of the unfractionated oil, *i.e.*, as it is distilled from the root, is 1·01 to 1·03. It is dextro-rotary, + 25° to + 40°, and should give a clear solution with 1½ to 2 volumes of 80 per cent. alcohol. Schimmel & Co. give the following figures for perfectly genuine samples of their own distillation :—

Specific gravity	1·019 to 1·027
Optical rotation	+25° to +26°
Ester number (as per cent. KOH) .	7 to 8
Solubility in 80 per cent. alcohol .	1 in 1½ to 2

A sample was fractionated with the following results :—

B. P. at 23 mm.	Per cent.	Rotation.
144°-164°	8	-4° 10′
164°-170°	10	-3° 20′
170°-180°	24	+2° 5′
180°-185°	30	+31° 40′
185°-200°	20	+47° 5′

From the point of view of the practical perfumer, this oil (which is worth from 8s. to 10s. per oz. when pure) is said to blend excellently with the odours of orris root and "cassie" flowers (*Acacia Farnesiana*).

The above-described are the Indian grass oils of which we possess reliable knowledge. The only ones in addition which need be here mentioned are the so-called "camel grass" oil, obtained by distilling the grass *Andropogon lanigerum*, and the oil from *Andropogon odoratus*. The camel grass grows freely on the lower Himalayas and in Thibet, and has been found in Beluchistan. Dr. Dymock distilled some of the fresh plant, and states that the yield was 1 per cent. According to Schimmel, the oil has an odour of elemi, a specific gravity ·915 to ·919, and is optically active from - 4° to + 34° 38′. It contains phellandrene, and boils between 170° and 250°.

The oil from *Andropogon odoratus*, which is obtained by distillation from the grass, has a specific gravity ·945 to ·950, and is laevo-rotary - 22° to - 23°. The yield is under ·5 per cent.

N. O. Aroideæ.

Calamus Oil.—This oil is distilled from the rhizome of the sweet flag, *Acorus calamus*. This plant is a member of a family with aquatic tendencies, and is probably a native

of Asia, although now found largely in Europe. Although the essential oil obtained from the rhizome is known either as *Ol. Acori calami* or *Ol. Calami aromatici*, the plant must not, as Pereira points out, be confused with the *Calamus aromaticus* described by Royle, which is one of the *Andropogon* family. The banks of European rivers afford a plentiful supply for the markets, and it is also cultivated in damp swamps in India. The fragrance of the plant and its oil appears to increase as the climate in which it is cultivated is warmer. Commercial rhizome of European origin is obtainable in the shops, and occurs as somewhat flattened pieces of about 4 inches long and about ¾ of an inch thick. Keeping does not improve it, nor does the process of decorticating it, as is often done for appearance sake. Many of the essential oil glands occur in the outer layers of the rhizome, so that the process of peeling naturally lessens the odour value. Dymock thus describes the Indian rhizome in his *Notes on Indian Drugs*: "The root stock occurs in somewhat tortuous, sub-cylindrical or flattened pieces, a few inches long and from ½ to 1 inch in greatest diameter. Each piece is obscurely marked on the upper surface with the scars, often hairy, of leaves, and on the under with a zig-zag line of little, elevated dot-like rings, the scars of roots. The root stock is usually rough and shrunken, varying in colour from dark brown to orange brown, breaking easily with a short, corky, fracture, and exhibiting a pale brown spongy interior. The odour is aromatic and agreeable, the taste bitterish and pungent." The powdered rhizome is used for sachet and toilet powder. From dried German rhizome, Schimmel obtained about ·8 per cent. of essential oil, whilst the fresh root yields from 1·5 to 3·5 per cent. Japanese root yields as much as 5 per cent. The oils do not quite agree in their chemical properties, and that from the green rhizome has a finer odour

than that from the dried. The chief difference noticeable, is that the oil from green root is more soluble in weak alcohol than that from the dried. But little is known of the chemistry of this oil. Kurbatow states that there is a large proportion of a terpene boiling at 158° to 159° present, which forms a crystalline hydrochloride melting at 65°. Its specific gravity was ·8793 at 0°. From the author's knowledge of this oil, this terpene was probably impure pinene. In addition to this there appear to exist a sesquiterpene and certain oxygenated constituents not yet identified; by distilling off the terpenes under reduced pressure, the residual oil has a specific gravity of from 1·000 to 1·018, which indicates the high specific gravity of the oxygenated constituents of the oil.

Schimmel & Co. give the following figures for eleven samples distilled by themselves:—

Specific Gravity.	Optical Rotation.
·970	+20° 44′
·962	+31°
·969	+18°
·967	+20°
·963	+15° 50′
·964	+16° 47′
·967	+17° 10′
·966	+27° 12′
·966	+13° 8′
·966	+22° 55′
·969	+15° 10′

These figures are almost sufficient to place the limits of, say, ·960 to ·970 for gravity and + 12° to + 35° for optical rotation. Oil from Japanese root, however, does not agree with these, as its specific gravity rises to 1·000, indicating its comparative freedom from terpenes. As a further test, all pure samples are soluble in all proportions in 90 per cent. alcohol. This oil is used extensively for the preparation of aromatic cordials and liqueurs, and also for perfuming toilet articles and snuffs. It is worth from 5s. 6d. to 6s. 6d. per lb.

from the wholesale houses. An oil is also distilled from the fresh leaves of the plant. The yield is from ·2 to ·3 per cent. of an oil of specific gravity ·965 and optical rotation about + 20°.

N. O. LILIACEÆ.

Garlic Oil.—This oil is distilled from the entire fresh plant *Allium sativum*. The average yield of oil, according to Schimmel, is about 1 oz. from a cwt. of the plants, although Wertheim obtained 3 to 4 oz. from this quantity. The oil is a liquid possessing the characteristic unpleasant odour of garlic, optically inactive, of specific gravity 1·045 to 1·060. It was examined by Wertheim, who stated that it contained allyl sulphide and allyl oxide. The most modern, and most trustworthy examination of the oil, however, is due to Semmler (*Arch. Pharm.*, ccxxx., p. 434). He states that the garlic yielded ·09 per cent. of oil of specific gravity 1·0525 at 14·5°. A small quantity of crystals was deposited when the oil was cooled in a freezing mixture. The oil contains no oxygen, and therefore no allyl oxide. When fractionated under a pressure of 16 mm., four main fractions were obtained. Fraction 1 (6 per cent.), consisted of allyl-propyl disulphide $C_6H_{12}S_2$, a bright yellow oil of specific gravity 1·0231 at 15°, and boiling at 66° to 69° at 16 mm. Its odour is that of onions. Fraction 2 (60 per cent.), consisted of diallyl disulphide, $C_6H_{10}S_2$, a light yellow oil of garlic odour, much resembling the last-named body, boiling at 78° to 80° at 16 mm., and decomposing at 150°. Its specific gravity is 1·0237 at 15°. Fraction 3 (20 per cent.), boiling at 112° to 122° at the same pressure, consisted of a body $C_6H_{10}S_3$, the exact constitution of which was not elucidated. Fraction 4 (10·5 per cent.), boiled above 122°. It contained still more sulphur, and corresponded to the empirical formula $C_6H_{10}S_4$. Semmler states that allyl sulphide, $(C_3H_5)_2S$, does not exist

in the oil, as originally stated by Wertheim. He also attributes to Beckett and Wright the statement that the oil contains a sesquiterpene, which he (Semmler) also contradicts. In this, however, Semmler is in error, as Beckett and Wright examined the sesquiterpene from oil of cloves (*Jour. Chem. Soc.*, 1876, i., p. 6), which was mistranslated into the *Jahresbericht* (1878, p. 398) as *Knoblauchöl;* hence Semmler's mistake, which is reproduced in Schimmel's report (*October*, 1893).

The oil has a very limited employment, and is rarely used medicinally, although it has been recommended for internal use as a tonic and stimulant to the stomach, and as a vermifuge; externally as a rubefacient. Its chief employment is for flavouring culinary preparations—a practice not in favour in England. It is worth from 12s. to 15s. per oz.

Oil of Onions is distilled from the bulb and fresh herb *Allium cepa.* The average yield of the plant is ·005 per cent. of an acrid oil of unpleasant odour and of dark brown colour. The oil has been examined by Semmler (*Archiv. Pharm.*, ccxxx., p. 443), who states that he obtained ·005 per cent. of oil, which contains no oxygen; its specific gravity was 1·041 at 9°, and its optical rotation − 5°. As it decomposes when boiled under ordinary pressure, it was fractionated at 10 mm. The chief portion of the oil consisted of a compound $C_6H_{12}S_2$, an oil of specific gravity 1·0234 at 12°, boiling at 75° to 83° at 10 mm. From the higher boiling fractions a substance was obtained, apparently identical with one of the constituents of oil of asafœtida. No allyl sulphide was found. The employment of this oil, which is somewhat disagreeable to manufacture, is quite similar to that of oil of garlic.

Allium Oil, from the fresh herb *Allium ursinum*, has a specific gravity 1·013, and contains various vinyl sulphides.

N. O. IRIDEÆ.

Orris Oil.—Three species of the Iris are used for the preparation of this oil. These are (*a*) *Iris germanica*, common in the districts near Florence, and also found in Central Europe, Northern India and Morocco; (*b*) *Iris pallida*, found in Istria, Florence and Lucca; (*c*) *Iris florentina*, occurring on the Macedonian coast, and near the coasts of the Black Sea, and also in the neighbourhood of Florence and Lucca. The finest roots are produced in the Tuscany district, and are known as Florentine orris root, but it must be remembered that *Florentine* root is not synonymous with the root of *Iris florentina*, but embraces the three varieties, which grow to the highest degree of perfection in this district. After the Tuscany root, the Veronese is most valued. The roots, or more correctly the rhizomes, exported from Morocco and East India are of very secondary value, and do not arrive in the market in very good condition. The plant used to be left entirely to itself to grow wild, but extensive plantations are now cultivated. The plants are grown on hills, generally on sunny open spaces, or between rows of vines. A dry calcareous soil is most suitable. The plants are left undisturbed for two or three years, when the harvesting commences. Locally the plants are known as *giaggiolo*. The fresh rhizome has very little odour, and must be carefully dried before being sent away. Certain changes appear then to set in and the odour develops.

The odour of the dried rhizomes resembles the delicate violet perfume, and the powdered substance is a usual constituent of *violet powder*. The earlier application of this delicate perfume was in the form of an alcoholic extract, often known as essence of violets. But non-odorous substances are also extracted from the root by alcohol, and the odour is not so delicate as that of the carefully distilled oil. The yield of oil is from ·1 to ·2 per cent.; but when the

rhizome is treated with dilute sulphuric acid, the starch granules are broken up and liberate more essential oil, but the odour is much impaired. The essential oil obtained from the plant is of a buttery consistence, and contains certain non-volatile fatty bodies which are carried over mechanically by the steam. Flückiger, who investigated this substance, showed that it consisted chiefly of myristic acid with traces of the true volatile oil. Our present knowledge of the oil, however, is chiefly due to Tiemann and Krüger. These chemists obtained the oil by extracting the roots with ether, and steam-distilling the residue left on evaporation. The non-volatile portion contains a little myristic acid, whilst the volatile oil contains a large amount of myristic acid and its methyl ester, oleic acid, an oleic ester, oleic aldehyde, and a body which is responsible for the characteristic odour which they termed irone. This body was separated in a pure state by converting it into its phenylhydrazone and decomposing this with dilute sulphuric acid. Irone $C_{13}H_{20}O$ is an oil almost insoluble in water, readily soluble in alcohol, etc., boiling at 144° at 16 mm., of specific gravity ·939 at 20°. It is dextro-rotary. In the pure form the odour is sharp and unlike violets, but when diluted it somewhat resembles the natural violet flowers. Tiemann and Krüger then attempted to synthesise irone, believing it to be the odorous principle of the violet flower (of which so small a yield is obtained as to render an exact examination almost impossible). Whilst they did not succeed in producing irone, they obtained an isomeric body, pseudo-ionone, by condensing citral with acetone, which on heating with dilute sulphuric acid is converted into another isomer, which they termed ionone. This body is the now well-known artificial violet perfume, so extensively used in the so-called violet scent and soaps. This will be further dealt with in a later chapter, when the chemistry of irone will also be referred to. Commercially,

the aspect of orris oil is very important. It is expensive, being worth from 18s. to 25s. per oz. as against double that price ten years ago. Its unique delicate odour will prevent it from being replaced by the more intense but less delicate odour of ionone, and further, it forms an excellent "fixer" for this artificial perfume, so that a judicious mixture of orris oil and ionone leaves little to be desired. Its employment in fine perfumery is, and has for many years been, very extensive. A quite liquid oil, from which the inodorous solid constituents have been removed is now on the market, but its very high price does not appear to be proportional to the increase in odour value.

N. O. Zingiberaceæ.

Ginger Oil.—This oil is the product of distillation of the rhizome of *Zingiber officinale*, a native of tropical Asia, which is also cultivated in both East and West Indies and in Africa, and to a small extent in Australia. Possibly, also, it is found in China, although the greater part of the "Chinese ginger" appears to be the product of *Alpinia Galanga.*

The rhizomes are sometimes imported in the soft juicy condition known as "green ginger," but the ordinary ginger of commerce consists of the dried rhizomes which have been picked when the stalks have withered, and are either washed, dried and scraped (*uncoated* or *white* ginger), or merely washed and dried (*coated* ginger). Sometimes it is bleached or limed before sale. The gingers of commerce are of widely different value, according to their place of origin, and the aroma and value of the oil naturally depend to some extent upon this. The Jamaica product is most highly valued. The oil, which is obtained to the extent of about 2 to 3 per cent., is a pale yellow to dark yellow liquid of characteristic aromatic odour and pungency. Its

specific gravity is from ·872 to ·885, and it is laevo-rotary − 25° to − 45°. Very little is known of the chemistry of this oil. Thresh in 1881 published a paper on the subject, but apart from the statement that the chief ingredient of the oil is a sesquiterpene or mixture of sesquiterpenes, little information of value was given. Schimmel & Co. (*Report*, April, 1894) have examined the terpenes of the oil and have identified phellandrene and camphene amongst them. The former was identified by its crystalline nitrite and the latter by its conversion into isoborneol. According to Thresh, the English distilled oil yields the following fractions on distillation :—

	Per cent.
Below 150°	5
150°-200°	10
200°-240°	8
240°-265°	60
265°-300°	7
Residue	10

These results yield but little information, however, as decomposition goes on to a slight extent during distillation at ordinary pressures.

A comprehensive examination of this oil is greatly needed.

The chief employment of this oil is for flavouring liqueurs and other beverages, but extracts of the rhizome are preferred on account of their greater pungency. The value of the oil is from 12s. to 15s. per lb. at present.

Galangal Oil.—This oil is obtained from the rhizome of *Alpinia galanga*, a plant cultivated in China and Siam, and from which the greater part of the so-called "ginger" of these countries is obtained; possibly also from *Alpinia officinarum.* The oil is obtained by moistening the ground rhizomes with water, and after some hours, distilling them with steam. The oil is of a greenish-yellow colour, with a sharp taste and pungent camphoraceous odour. The yield is from ·5 to 1·5 per cent. The specific gravity varies

from ·915 to ·925, and the rotation from − 1° to − 4°. The only constituent which has been identified with certainty is cineol (eucalyptol), of which it contains a large proportion. According to Dragendorff, the oil should not be quite soluble in an equal volume of 85 to 90 per cent. alcohol. He states that the chief adulterants are oils of pimento and cloves, which are much more soluble in alcohol. The ready solubility of samples of oil in all proportions of 80 per cent. alcohol is, therefore, probably indicative of adulteration. Oil of lemon and turpentine are also used to sophisticate the pure oil. These will be indicated by the lowering of the specific gravity and the alteration in the optical rotation. This oil is worth about four times as much as a fair quality ginger oil.

Cardamom Oil.—The oils form different kinds of cardamoms, and although similar in general properties, differ to a certain extent chemically. The seeds from which the oil is distilled are chiefly exported from South West India and Ceylon in their pericarps, forming the cardamoms of commerce. The *British Pharmacopœia* of 1885 prescribed Malabar cardamoms, but the 1898 *Pharmacopœia* is less stringent, and there are three chief varieties agreeing with the new description. According to the *Chemist and Druggist* (*Diary*, 1899, p. 500), the following are their chief characters :—

"*Mysores.*—Divided into rounds and longs. The former are what the *B. P.* calls 'ovoid'; they vary in length from ¼ inch to ⅘ inch (the latter 1 in 10), and have a smooth pericarp of a cream colour, due to the use of bleaching agents. Their quality is judged by their weight. Sometimes the seeds are shrivelled (unripe), so that the fruit is husky. This is not so frequent in the longs, which are simply thinner than the rounds, and are not so smooth on the surface, nor so pale, as a rule. The *B. P.* description, 'longitudinally striated,'

might exclude most of the rounds, as they look smooth until closely examined.

"*Malabars.*—These are smaller than Mysores, and there is a greater proportion of seed to pericarp in them. They are fat pods, with a pointed apex. Generally pale brown or pink and longitudinally striated. Rarely more than ½ inch long. They have a full flavour.

"*Mangalores.*—These are almost globular in shape and not unlike Malabars. All three are washed or bleached before exportation.

"*Seeds.*—A goodly proportion of cardamoms come straight into the market freed from their pericarps. The *B. P.* excludes these because they are supposed to lose flavour on keeping. Wholesalers and large manufacturers use them when fresh; fine brown seed is as strong as the kind just freed from the pericarps. Grey seeds are inferior."

It is fairly certain that the plant *Elettaria cardamomum* produces most of the ordinary cardamoms, whilst the "Ceylon wilds" are the product of a variety of this plant, known as *variety β*. The majority of the cardamoms of commerce are imported from Ceylon, and may be described as *Ceylon-Malabars* or *Ceylon-Mysores*, according as they fit in with the above descriptions. The Ceylon wilds are mostly consumed in the manufacture of a certain cake made in South Germany, and are not an ordinary article of commerce. Some confusion exists as to the botanical characters of some of these seeds, and more so as to the essential oils they yield. The oil is usually distilled from Ceylon seeds, which yield from 3 to 6 per cent. of oil. According to Weber, cardamom oil contains terpinene, and another terpene (either limonene or dipentene) and terpineol. According to Schimmel, the oil derived entirely from Malabar cardamoms (*Elettaria cardamomum*) is obtained to the extent of from 4 to 8 per cent. of the seeds used. Its specific gravity was ·943 and its

optical rotation + 34° 52′. It dissolved in 4 parts of 70 per cent. alcohol. It was found to require 13·2 per cent. of potash for saponification, thus indicating a very high ester content. The esters were chiefly those of acetic acid. Whilst no terpinene was found in the oil, a considerable amount of cineol and dextro-rotary terpineol were detected. The chemistry of these oils still requires considerable elucidation. Samples of oil distilled from both Malabar and Mysore (Ceylon) seeds, obtained from authentic sources by the author, showed that there was practically no difference between the two oils, although Schimmel states that Ceylon cardamom oil has a specific gravity of ·895 to ·910 and a rotation of + 12° to + 13°. Possibly the oil from the wild cardamom is here meant.

The Ceylon-Malabar seeds yielded 1·3 per cent of oil, and the Ceylon-Mysores 2·6 per cent. Both were bright yellow liquids, whose odours were scarcely distinguishable. The specific gravities and optical rotations were as follows:—

	Sp. Gr. at 15·5°.	Optical Rotation at 16° (100-mm. Tube).
Oil of Malabar cardamoms . .	0·9418	+ 40° 41′
Oil of Mysore cardamoms . .	0·9418	+ 46° 39′

These figures are in fair agreement with those given for Malabar oil, but in no way resemble those quoted by Schimmel for Ceylon oil, which are difficult to understand.

The oils were soluble with a slight opacity in 40 to 45 volumes of 60 per cent. alcohol.

Little difference exists between the two oils. On distillation at ordinary pressure the oil, which is very rich in esters, in both cases decomposes partially, and a considerable quantity of free acid distills over. According to Weber (*Annalen*, 238, 89), formic and acetic acids are found in the distillate.

Acetic acid is undoubtedly the chief acid constituent of the esters, but the author is unable to confirm the presence of formic acid. If it is present, it is only in faint traces. On distillation under reduced pressure the earlier fractions (the boiling point rises gradually until 50 per cent. has distilled over) contain cineol, but only to the extent of 5 to 10 per cent. of the oil. This figure is the result of an approximate estimation by means of phosphoric acid. The earlier fractions also contained one or more terpenes, amongst which was limonene. Weber states that terpinine is also present, but the author was unable to identify this hydrocarbon, nor could Schimmel find it in Malabar oil; and as it easily forms a well-defined nitrite when present, it cannot exist in an appreciable quantity. A small quantity of terpineol is present in both oils, and is easily identified by its phenylurethane. Schimmel states that it is an optically active modification. The terpineol comes over with the fraction obtained at 160° to 170° C. at 18 mm. The nature of the alcoholic constituent of the greater part of the esters requires further elucidation.

In addition to the above, the following varieties of "cardamom" oil have been described: *Korarima Cardamom Oil* is the product of *Amomum korarima*. The yield is about 2 per cent., but the oil has not yet been examined.

Kameroon Cardamom Oil.—The fruits from which this oil is obtained are identical with the Madagascar cardamoms. They are derived from *Amomum danielli*. The yield of oil was 2·33 per cent., its specific gravity was ·907, and its optical rotation − 20° 34′. The oil is soluble in 7 to 8 parts of 80 per cent. alcohol. It contains cineol and possesses an odour which prevents its being employed as a substitute for the ordinary oil.

Siam Cardamom Oil.—This oil is distilled from the seeds of *Amomum cardamomum*, which are known on the market as camphor seeds on account of their camphor-like odour.

II. DICOTYLEDONS.

(A) *Monochlamydeæ.*

N. O. PIPERACEÆ.

Oil of Cubebs.—This oil, which is official in the *British Pharmacopœia*, is distilled from the fruit of *Piper cubeba* (*Cubeba officinalis*, Miq.). The cubebs of commerce are the dried unripe fruits, which resemble ordinary black pepper in appearance, except that they are rather lighter in colour; they are chiefly imported from Java.

The berries are coarsely ground and distilled with steam, yielding from 10 to 18 per cent. of volatile oil. This is of a greenish or greenish-blue colour, and of very characteristic and somewhat aromatic odour. The colour has been stated to be due to copper, but this is erroneous, as the higher fractions contain a blue oil in greater or less quantity, which determines the tint of the liquid. The specific gravity varies from ·910 to ·930, and the optical rotation from − 30° to − 40°, usually about − 32°. The chemistry of this oil is in need of further elucidation, as it is clear that there are several constituents present which have, so far, escaped identification. The terpene dipentene is present, and the sesquiterpene cadinene, probably together with another sesquiterpene. There is also present, especially in the oil distilled from old fruit, which has doubtless become partially oxidised, a small amount of the so-called cubeb-camphor. This body, $C_{15}H_{25}OH$, appears to be a crystalline sesquiterpene alcohol derived from the sesquiterpenes (or one of them) by oxidation. From a mixture of ether and alcohol it crystallises in rhombs, melting at 65° and boiling at about 245° with decomposition. The nature of the blue oil found in the higher fractions is unknown. Fractionation yields useful information in the examination of the oil, and although the quantities obtained at various temperatures are not

constant, the following represents an average sample, distilled from an ordinary Wurtz flask. The oil commences to boil at about 170° to 180° and there passes over:—

	Per cent.
Below 250°	10
250°-260°	25
260°-270°	50
270°-280°	5

These results will indicate the absence of turpentine. The oil is soluble in from 1 to 2½ volumes of 90 per cent. alcohol.

Few oils have varied so largely in price during the past ten years as this. Ten years ago it was worth from 40s. to 50s. per lb. To-day it can be bought of absolute purity at from 4s. to 5s. Over-production is partially responsible for this, but at the same time, the use of the oil in medicine is becoming much less common than it was formerly. As a drug it is valued on account of its action on the urinary organs, but in this respect it has largely given way to santal oil and balsam of copaiba. It is employed also to a small extent to flavour certain liqueurs.

Matico Oil.—This oil is distilled from the leaves and spikes of *Piper angustifolium* (*Artanthe elongata*, Miq.), a plant indigenous to tropical America. The yield of oil is very variable, from less than half per cent. to 3·5 per cent. The oil is a liquid of somewhat penetrating odour, of specific gravity ·93 to 1·07, and optical rotation about + 5°. Very little is known of the chemistry of the oil. There is present a small quantity of "matico camphor," a crystalline odourless solid of specific gravity 1·080, melting at 94° and strongly laevo-rotary. Its formula is $C_{12}H_{20}O$, and it has been suggested that it is the ethyl derivative of ordinary camphor, but there is no experimental evidence in favour of this. Schimmel & Co. state that they have found asarone $C_{12}H_{16}O_3$ in one sample of the oil, which had the high specific gravity 1·077 and was slightly laevo-rotary.

The oil, which is employed in medicine to a small extent, is often adulterated with alcohol and turpentine, on account of its high price. Its commercial importance is not great.

Betel Oil is distilled from the leaves, either fresh or dried, of *Piper betle* (*Chavica betle*, Miq.). The yield is from ·5 to 1 per cent. Eykman investigated the oil some years ago and stated that it contained the phenol, chavicol (*q.v.*), several terpenes, a sesquiterpene and possibly cymene and cineol. He described it as a yellowish-green oil, with a burning taste, and peculiar, pleasant odour. It was stated by him to be laevo-rotary. Bertram and Gildemeister, however, in 1890, distilling the oil from the dried leaves, stated that the oil contained 70 to 75 per cent. of betel-phenol, which was found to be a methoxy-chavicol. They identified the sesquiterpene as cadinene. Schimmel states that the oil distilled from leaves from all sources contained this betel-phenol, and in addition the oil from Java leaves contained several terpenes and chavicol, and that from dried Siam leaves contained a sesquiterpene, and that from Manila contained betel-phenol, but no chavicol. They give the specific gravities as follows. Dried leaves, Bangkok, 1·034; fresh leaves, Java, ·958; fresh leaves, Manila, 1·044. The optical rotation is given as + 2° 53′. This oil is of no commercial importance.

Pepper Oil.—This oil is distilled from the unripe berries of *Piper nigrum*. The yield of oil is from 1 to 2·5 per cent. The oil is often of a greenish colour, somewhat resembling oil of cubebs, but with a much more pungent odour. The green colour is due to a high boiling constituent, possibly identical with that in oil of cubebs. According to Eberhardt, the specific gravity is ·8735 and the rotary power − 3° 12′. The oil was shown to consist of a terpene (probably phellandrene), and one or more sesquiterpenes. Schimmel gives the specific gravity as ·880 to ·905 and the optical rotation

as - 5°. An oil is also obtainable from the long pepper, *Piper longum*. This pepper yields 1 per cent. of a thick pale greenish oil, of specific gravity ·861, boiling chiefly between 250° and 300°.

A *Pepper Oil* is obtained from the fruits of the Javanese plant *Piper Lowong*. The oil obtained by direct distillation of the powdered fruits with steam has a specific gravity of about ·860, whilst that obtained by distilling the ethereal extract has the high specific gravity ·925. A sesquiterpene appears to be present, and a crystalline body melting at 164°, which is probably a sesquiterpene alcohol.

N. O. Urticeæ.

Oil of Hops.—This oil is distilled from the flowers of the ordinary hop, *Humulus lupulus*, which yield from ·3 to 1 per cent. The oil glands are situated under the scales of the flowers (catkins); these grains or glands can be separated from the flowers, and are known in commerce as lupulin. The quality of the oil is, of course, dependent on the state of the flowers, and when the crops have had to be "sulphured," the oil obtained from the flowers is less valuable and contains traces of sulphur. The pure oil has a pale yellow to faint green tint, but can be obtained colourless by rectification. It has a penetrating hop odour. Several authorities give the specific gravity as high as ·908 to ·910, but Schimmel gives ·855 to ·880 as the extreme limits. The oil is usually dextro-rotary, but seldom exceeds + 1°. Several chemists have investigated this oil. In 1822, Payen and Chevalier stated that there were at least two bodies present. Wagner in 1853 obtained a terpene boiling at 175° and an oxygenated body which yielded valeric acid on oxidation. Personne (*Jour. Pharm.*, xxvi., p. 241, and xxvii., p. 22) obtained a dextro-rotary terpene of specific gravity ·888. The most modern and reliable investigation, however, is due

to Chapman. Four samples of authentic origin gave the following figures:—

	Sp. gravity at 15°.	*Rotation* [α]ᴰ.
1	·8802	+ 0·41′
2	·8662	+ 0·58′
3	·8771	+ 0·50′
4	·8743	—

All these samples were free from sulphur and neutral to litmus. No ketones or aldehydes were detected in the oil. A prolonged series of fractionations at 60 mm. pressure yielded the following fractions: (1) 89° to 91°; (2) 145° to 150°; (3) 163° to 168°; (4) 168° to 173°. The first and fourth were the main fractions, the second and third being very small. Fraction No. 1 was a colourless oil, practically unacted upon by sodium. When distilled from this metal, it boiled at 86° to 89° at the same pressure. Under ordinary pressure it boiled at 166° to 171° almost entirely, but towards the end, the temperature went up to 250°, due to polymerisation of the original substance. The specific gravity at 20° was found to be ·799 and the rotation − 0·56′. It is clear that this body is not a terpene, and Chapman's experiments lead him to consider it as a mixture of tetrahydrocymene, and one of the so-called "olefenic terpenes," bodies as yet but little understood. Fraction No. 2 was a liquid of specific gravity ·885, and may be geraniol. Fraction No. 3 was a mixture of 2 and 4. Fraction No. 4 was found to be a sesquiterpene, to which the name humulene (*q.v.*) was given. For further details of the chemistry of this body, which constitutes the greater part of the oil, see the original papers (*Chem. Soc. Proc.*, 1893, p. 177, and *Jour. Chem. Soc.*, 1895, pp. 54 and 780). This oil, which is very expensive, is used to some extent in the brewing industry, both to add flavour to beer and to give a good odour to poor and damaged hops.

Hemp Oil.—The flowers of *Cannabis sativa* yield about

$\frac{1}{10}$th per cent. of volatile oil of specific gravity about ·930. It is laevo-rotary to the extent of about − 10° to − 12°. The oil appears to consist entirely, or nearly entirely, of sesquiterpenes and terpenes.

Indian Hemp Oil is obtained by subjecting the flowering twigs of *Cannabis Indica* to steam distillation. The resulting oil is of thin consistency, and possesses an agreeable aromatic odour. It boils between 248° and 268°. Its specific gravity is about ·930, and it appears to consist chiefly of a sesquiterpene, which has been named cannibene.

N. O. Myricaceæ.

Myrtle Oil.—The leaves of *Myrica cerifera*, the wax myrtle, yields about ·02 to ·05 per cent. of an essential oil of specific gravity about ·885 and optical rotation − 5°. The leaves of the bog myrtle, *Myrica gale*, also yield a small quantity, under 1 per cent., of oil of agreeable odour. Its specific gravity is about ·870. It contains a large quantity of stearoptene, and solidifies at about 11°. The chemistry of these oils is practically uninvestigated. (These plants must not be confused with the true myrtle, *Myrtus communis*, which will be referred to later.)

Sweet Fern Oil.—The leaves of *Comptonia asplenifolia*, another plant of this natural order, yield about $\frac{1}{10}$th per cent. of an essential oil of specific gravity ·926.

N. O. Salicineæ.

Poplar Oil.—The young buds of the black poplar, *Populus nigra*, yield from ·3 to ·6 per cent. of oil of a pale yellow colour somewhat recalling the odour of chamomiles. According to Schimmel, its specific gravity varies from ·900 to ·905. Picard gives ·9002 as the specific gravity of a sample he examined, and stated that it consisted chiefly of a hydrocarbon $C_{20}H_{32}$, was dextro-rotary, and boiled at 260°.

N. O. Chenopodiaceæ.

Chenopodium Oil.—This oil is also known as American wormseed oil (*not to be confused with true wormseed oil, the product of Artemisia absinthium, one of the Compositæ*). It is distilled from both the fruit and the whole herb of *Chenopodium ambrosioïdes*, var. *anthelminticum*, the fruit yielding about 1 per cent., and the herb ·3 per cent. of oil. The specific gravity of the fruit oil is from ·900 to ·975, and of the herb oil about ·900. According to Schimmel (*Report*, 1893), samples of fruit oil from absolutely reliable sources have a specific gravity of about ·970, and are soluble in 10 volumes of 70 per cent. alcohol. The fruit oil is laevo-rotary, from − 5° to − 18°. The herb oil has an odour recalling trimethylamine, but nothing definite is known of its chemistry.

N. O. Laurineæ.

Cassia Oil.—This oil is distilled from the leaves, twigs and other parts of the plant *Cinnamomum cassia*, which is probably a native of Cochin China, but which is chiefly cultivated in China proper, the three chief districts being Taiwu (*Lat.* 23° 34′ N., *Long.* 110° 18′ E.), in the Kwangsi province; Lukpo (*Lat.* 23° 6′ N., *Long.* 112° 24′ E.), and Loting (*Lat.* 22° 52′ N., *Long.* 111° 8′ E.), both in the Kwangtung province. Much confusion and mystery existed till recently in regard to the exact botanical source of the plant and the nature of the oil and the methods of its distillation, etc., which were largely brought about by the shameful adulteration by the Chinese. The following details given by actual observers will give the most reliable information on much affecting these questions. In a *Report on a Journey to Kwangsi*, by H. Schroeter, 1887, the writer says:—

"The shrubs destined for the production of the *Cassia lignea* proper are partly stripped during the summer months

of their minor branches and exceptionally juicy leaves. They are then conveyed in huge bundles into the valley, where they are boiled in large vessels. From the aromatic juice thus obtained the esteemed cassia oil is recovered by means of a most primitive distilling apparatus. As the Li-kin stations on the road to Canton levy an excessive duty upon the oil, in addition to that exacted by the Imperial Customs, the oil is carried in tins across the hills to Pakhoi and thence transported to Hong-Kong, *viâ* Macao, instead of reaching Canton by the waterway, intended by nature for its conveyance."

These statements are in agreement with those contained in a report presented to the Hong-Kong Government by Mr. Charles Ford, which will be found reprinted in the *Journal of the Linnæan Society*, December, 1882, and in which much valuable information is given. More recently (1895), Messrs. Siemssen and Co. of Hong-Kong, on whose behalf Herr Schroeter's visit was made, sent a representative, Mr. Struckmeyer, to the Loting-Chow districts, in company with the German consul, Dr. Knappe. The report of these travellers is sufficiently interesting to warrant its reproduction here. For it, the author is indebted to Messrs. Schimmel & Co. It reads as follows:—

"We embarked on the right bank of the West river, opposite Tack-Hing-Chow, at six A.M. on the 15th of December, 1895. We left there our large boat and went to a place with extensive matting factories, located on the Loting-Chow or Lintau river, arriving there about half-past two o'clock in the afternoon. Next morning we continued our march to Loting-Chow, under the guidance of a Chinese, a manager of one of the largest matting establishments in Lintau. We were attended by a servant of the consul, who also served as interpreter, and by several Chinese coolies. After a brisk march we took up our quarters in a small

Chinese temple, and made strolls through the city, which, although small, seems to be a busy trading place. Loting-Chow is pre-eminently a centre for all the products of the cassia tree, and for firewood to be shipped thence to Canton and Macao.

"The cassia plantations are still further inland, and we had to defer visiting them until the next day, because they were too far off, according to our informants in Loting-Chow. They proposed, however, to accompany us the following day to cassia plantations as well as to a distillery. During the afternoon we visited a dealer in cassia oil, the only one in the place, he pretended. Subsequently, on our return, we ascertained this statement to be false. At first he was very reticent, but subsequently yielded to some pressure. He possessed a separating funnel, a syphon, test-tubes, etc., as recommended by Messrs. Schimmel & Co. in Leipzig, and pretended to examine all oils offered to him for sale, because he had been condemned, as he said, to $900 damages for inferior cassia oil sold by him some five years ago. He assorts the commercial oil into four to five grades, but deals only in the three best qualities, unadulterated in his opinion. He had in stock but a small quantity of the best oil, and gave us small specimens of three kinds of his oil, of which I shall treat more fully further on.

"Although everything was arranged for the next day with our Chinese guides, we had to face considerable difficulties. During the evening we were informed that a certain 'Mr. Wong' (who never appeared in person) had arrived from the interior, and reported that a visit to the cassia plantations would be of no use, and that it would not be possible to inspect any distillery, because some children had been instructed by thieves to steal the leaves from the cassia trees, and that in consequence a brisk contest between the owners and the thieves was in progress. Besides, it

was claimed that only one distillery existed, at a distance of 20 Lis (about 8½ miles), and that this was not in operation in consequence of the disturbances. This wondrous story, and the circumstances under which it was imposed upon us, convinced us that it was an impudent lie, or, at best, an absurd exaggeration. The more they tried to dissuade us from continuing our trip, the more we persisted upon the realisation of our plan. Finally the Lintau Chinaman volunteered to accompany us to the plantations, but would not make any promise in regard to visiting any distillery. The departure was fixed for six o'clock the next morning. We were in a peculiar position, since our interpreter also appeared to antagonise our aims; nor had we any time to lose in order to comply with all other arrangements of our expedition.

"The next morning, 17th December, we and our men were ready at six o'clock, but the two Chinese failed to appear, although we had requested them several times to hurry. We were waiting with our attendants in front of the temple when messengers brought the idle excuse that the two Chinese had not yet received their breakfast, and that no carriers for our baggage could be obtained. At a quarter to eight we sent word that we would start without guides, and when they caught up with us at ten o'clock we paid no attention to them.

"We finally succeeded in inducing one of the many onlookers to guide us to one of the distilleries. The march went on very slowly, and the actions of our interpreter led us to foresee further intrigues. As on the previous day, our route passed through a hilly country with numerous side valleys and little ravines. After having passed a number of hills covered with young cassia trees, we reached a distillery by ten o'clock, but found out that it was not in operation. We were again told that this was the only distillery in the

neighbourhood. But as luck would have it, during our brief stay a small trader appeared upon the scene and offered some thick cassia bark for sale. By small purchases and promises we succeeded in inducing the man to lead us to another distillery, and one in operation.

"We returned the same way by which we had come, and at noon-time arrived at a distillery in full operation. It was a little off the road, but was much nearer to our starting point in the morning than the distillery to which we had been led at first. We met with a very kind reception by the owner and his employees, and they readily gave us any desired information. We ascertained that about twenty distilleries existed in this immediate neighbourhood, and that most of them at the time were in full operation. We subsequently found out on our return to Canton that a few slight disturbances had occurred in the cassia districts, but the fact remained that we had been treated to absurd stories and gross lies, probably at the instigation of some dealers in Loting-Chow.

"The distillery, like all others, is located in a ravine abounding in springs which furnish an ample supply of water for coolers. The distillery with all its arrangements closely resembles the one which some time ago was described and illustrated in one of the Reports of Messrs. Schimmel & Co.

"An iron pan is securely placed in a brick hearth with a large fire-place; upon this pan a large wooden cylinder lined with sheet iron is placed, upon whose upper rim a large cover of strong sheet iron rests. The space between the cylinder and the cover, around the rim, is made tight by strips of moist cloth or rags. Around the lower side of the cover there runs an outer groove for gathering and drawing off the water serving for cooling, and a narrow interior groove for collecting the distillate containing the essential oil. This distillate passes into tin cans and the oil collects at the bottom.

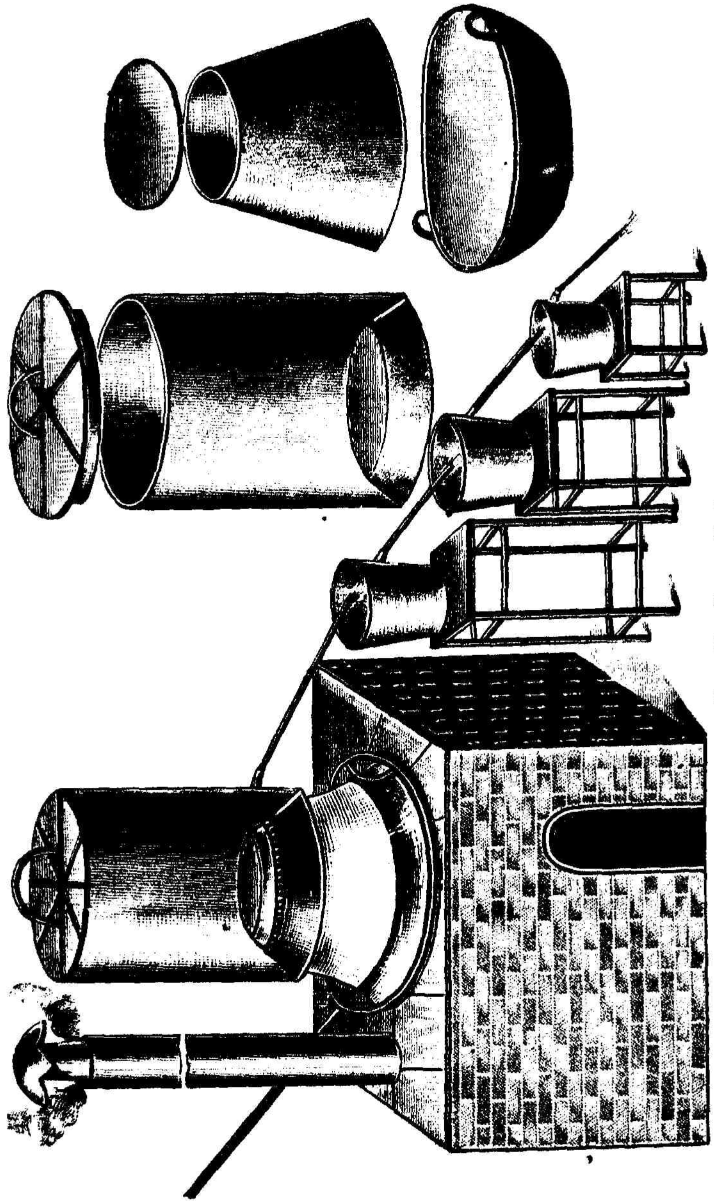


FIG. 14.—CASSIA STILL.

"At each charge of the cylinder, about 1 picul of leaves and twigs and 250 catties (= 2½ piculs) of water are employed; the water used is mostly from preceding distillates. The distillation lasts about 2½ hours.

"The yield of one such charge, when consisting of leaves only, is 1½ to 2 taels, and when consisting of 70 per cent. of leaves and 30 per cent. of twigs, 2½ to 3 taels of oil[1]. The oil obtained from leaves alone is in general the superior one.

"With a still of this capacity, as much as 50 catties of oil are obtained per month, or 3 to 5 piculs per year. The festivities connected with the Chinese New Year cause an interruption of the distillation for one or even two months. The quality of the oil depends upon the material used for distillation. Both too old and too young trees furnish leaves less rich in oil; large leaves are better than small, young ones; this explains the fact that the twigs and leaves gathered in spring and in winter yield an inferior oil to those gathered in midsummer and in autumn.

"The distiller who furnished us this information claims to produce but 1 grade of oil, using 70 per cent. of leaves and 30 per cent. of twigs. A specimen, marked A, was taken by us from the apparatus. The tin can contained but a small amount of oil resting under the water, and the sample, collected in a rather primitive way, contained some water. On standing, some drops of water separated at the top of the slightly yellow oil. It was subsequently examined by Mr. E. Niedhardt in Hong-Kong with the following result:—

"Specimen A (1895). A turbid liquid, which on standing separated into two layers, the upper one water, the lower one cassia oil of a light Rhine wine colour.

Consistency: very limpid.
Odour: the true oil of cassia, somewhat smoky.
Taste: the same.

[1] 16 Taels = 1 Catty = 605 Grammes; 1 Picul = 60 Kilos 500 Grammes.

Spec. grav.: 1·059.
Residue of distillation: 3·75 per cent.; resinous, sticky.
Cinnamic aldehyde: 86 per cent.
Solubility in alcohol 80 per cent.: complete.
Solubility in solution of sodium salicylate: complete.
Reaction with lead subacetate: no turbidity.

"The result of this investigation indicates that a rather large proportion of twigs seems to be required to materially reduce the quality of the oil. Perhaps twigs too old and too thick have a detrimental effect upon the quality of the distillate.

"The oily water, as collected during the process of distillation, is milky. Specimen B represents this water as separated from the oil and mixed with Specimen A.

"Specimen C represents the ready oil as our distiller sends it to Loting-Chow for sale. The specimen was taken from a tin can by ourselves.

"For these samples we were charged in proportion to the regular price of $600 per picul.

"The distillers generally purchase the leaves and twigs and carry on the distillation on their own account; occasionally they rent their stills to the owners of the raw material, mostly planters, or they run their stills on the latter's account in return for a compensation.

"In Loting-Chow we obtained two more samples of commercial oil. Specimen D was said to be a good oil of prime quality obtained from old leaves and commanding a price of $600 per picul. It did not change when brought into contact with water, but separated into smaller or larger globular masses, showing a few oil drops on the surface. It was of a light colour.

"Specimen E, said to be distilled from young leaves; price $580 per picul. It showed in water a more compact mass with a thin, transparent surface, and more oil drops on top of the water.

"Specimen F was said to have been obtained from old and young leaves and to have been adulterated with kerosene, and therefore to be of no use to the dealer; price $550. When brought into water, this oil formed a compact mass with a thick surface, partly of a whitish and striped appearance. Colour rather dark. The dealer stated that he had showed us this oil only as a specimen of adulterated oil, that he kept it only as a sample and that he had only a small amount of it. Consequently he could only sell us such a small sample.

"The adulteration is charged by every one to somebody else. We found no suspicious material in the distilleries, there is an abundance of pine leaves growing in the region, but their admixture to the cassia leaves was peremptorily denied; nor did we find any such admixture in the contents of the still examined by us. Although a few distillers may be guilty of dishonest practices, there is no reason to assume that the majority resort to deliberate adulteration by the admixture of foreign matter to the cassia leaves and twigs. On the other hand, we may conclude from the existence of adulterated oil in Loting-Chow, and from our examination made there, that the sophistication ought not to be imputed exclusively to the Chinese of Macao and Hong-Kong, if at all. The fact is, before the oil is sold to the foreign exporters, it comes from an extensive district and passes through so many hands that it is impossible to determine where and how it is actually adulterated. In Loting-Chow it was alleged that most adulterations are committed in the province of Kwang Si, where ten or even more qualities of cassia oil can be had.

"The question may here be raised whether the present methods of examination suffice to detect the most artful and subtle adulterations, as also whether the Chinese really possess the requisite knowledge and skill for such refined forms of sophistication.

"Sample A bears sufficient evidence that excellent oil can be, and is, produced. This detailed account, however, may indicate what difficulties the foreigner has to meet with when trying to get at the bottom of facts.

"Incidentally it may be added that the residue of the leaves and twigs, after having been dried, is used as burning material. The remaining ashes are subsequently extracted by hot water, and a kind of potash called Kamalni is obtained therefrom.

"Consul Dr. Knappe has forwarded a collection of the samples A, B, C, D, E and F and an elaborate report to the Foreign Office in Berlin. Sample A is the only one which we had examined in Hong-Kong."

Much credit is due to Messrs. Schimmel and Co. for the thorough way in which they have dealt with the cassia oil question, not only in connection with their efforts to combat the enormous adulteration practised by the Orientals, but in regard to their investigations of many of the difficult points existing in reference to this oil. They have obtained specimens of raw materials of various parts of the plant and examined the oils yielded by them. The results of their investigations are summarised as follows:—

"*Cassia Budsticks*.—Small, thin stalks, about 1 mm. thick and 5 mm. long, which possess a strong and pure cinnamon taste. Six hundred and fourteen kilos distilled by us yielded 10 kilos 120 gr., or 1·64 per cent. of a beautifully bright oil with excellent sweet taste, indicating a high percentage of aldehyde.

"We determined the specific gravity to be 1·0463, the aldehydic contents 92 per cent.

"*Cassia Leaves*.—The dried, leather-like leaves of the cassia plant with the strong petioles and small twigs. On mastication of leaves and petioles separately, both communicated a faint but pure taste of cinnamon, whilst the twigs exhibited strong cinnamon taste.

"In order to obtain exact results we caused a certain quantity of the material to be sorted into leaves and stalks. One hundred kilos material yielded—

Leaves	85 kilos
Small twigs . . .	15 „

"On distillation the leaves yielded a beautiful, sweet tasting oil, with specific gravity 1·056 at 15° C. The aldehydic contents were determined as 93 per cent.

"The thin twigs showed a less percentage of essential oil than the leaves, but this possessed a similar sweet taste to the oil from the leaves. The specific gravity was 1·45 at 15° C. The aldehyde amounted to 90 per cent.

"The following parts of the cassia plant have been distilled by us with the appended results:—

1. The Cassia bark (the *Cassia lignea* of commerce).
   Yield of essential oil: 1·5 per cent.
   Aldehyde in oil: 88·9 per cent. Specific gravity 1·035.
2. The Cassia buds (the *Flores cassiae* of commerce).
   Yield of essential oil: 1·550 per cent.
   Aldehyde in oil: 80·4 per cent. Specific gravity 1·026.
3. Cassia budsticks.
   Yield of essential oil: 1·64 per cent.
   Aldehyde in oil: 92 per cent. Specific gravity 1·046.
4. Cassia leaves, leafstalks and young twigs mixed.
   Yield of essential oil: 0·77 per cent.
   Aldehyde in oil: 93 per cent. Specific gravity 1·055.

"Nos. 1 and 2 are completely excluded as raw materials for the preparation of cassia oil on account of the price.

"No. 3 is also out of the question, because the value, about $4 per picul, is still higher than that of broken cassia and because the yield would not be sufficient.

"It can, therefore, be assumed with safety, that the cassia oil of commerce is distilled in China from the leaves, leafstalks and young twigs of the cassia plant, probably together with various refuse products worthless for other purposes."

The ordinary commercial oil of cassia, which is imported from Hong-Kong, etc., in cases containing four cans, each

holding about 16½ lbs., may be regarded as distilled chiefly from the leaves and twigs. The grosser adulterants, which are far less common to-day than they were a few years ago, are colophony, petroleum and fatty oils. Low grade oils are found in commerce, which have not, so far, been positively ascertained to be adulterated. Possibly they are the product of a variety of the plant, or they may be adulterated with some oil we do not yet know of.

The main constituent to which the odour of this oil, and of oil of *cinnamon* is chiefly due, is cinnamic aldehyde. Small quantities of cinnamic acid, its oxidation product, are naturally found in the oil, the amount varying according to its age. A terpene, a compound of cinnamic and acetic acids, and cinnamic acid esters, also exist in very small quantities. A stearoptene was also found in this oil in 1850 by Rochleder. According to this chemist its formula is $C_{28}H_{29}O_5$. But a recent investigation by Bertram and Kursten shows that it is *ortho*-methyl-coumaric aldehyde $C_6H_4(OCH_3)(CH : CH.COH)$. The oil when pure should have a specific gravity of from 1·050 to 1·065. Its optical activity should be almost *nil*, never more than 1° either way. It should dissolve completely in 3 to 4 volumes of 70 per cent. alcohol, a characteristic which is interfered with by adulteration with colophony, petroleum, or gurjun oil. The following rough method gives an approximate estimate of the amount of adulteration, if this is colophony, heavy petroleum oil or a fixed oil. Weigh 50 grammes of the oil into a small Wurtz flask, and connect in the usual way to a condenser, and gradually heat with a naked flame. The oil commences to boil at about 210°, and the bulk distils over between 240° and 260°. When the thermometer rises to 280° and white vapours rise the distillation is stopped.

On cooling the flask (whose weight is known) its contents are weighed; the residue should not exceed 10 per

cent.—it is seldom more than 8 per cent.—and should not solidify. Over 10 per cent. residue indicates adulteration, and if this residue solidifies colophony is present. The most important method of examination, however, is the determination of the percentage of cinnamic aldehyde, and upon this percentage commercial oils are always sold on the market. In this process the following details should be observed. Ten c.c. of the oil are run into a Hirschsohn flask (capacity about 100 to 150 c.c., with a neck about 5 inches long and ¼ inch in diameter, graduated in $\frac{1}{10}$th c.c.). The flask is then filled about ¾ full with a 30 per cent. solution of sodium bisulphite, and the whole well shaken. The flask is then placed on the water bath for several hours with occasional shaking, until the precipitated compound of the aldehyde and bisulphite is completely dissolved, and only a clear oil floats on the surface. Bisulphite solution is then carefully poured in until the oil is driven up into the neck, and when it has attained the temperature at which the oil was measured, the amount is read off. This gives the percentage of non-aldehydic constituents, the difference being returned as cinnamic aldehyde. Pure oils should not give less than 75 per cent. of aldehyde, the best oils yielding 80 to 85 per cent., or occasionally even higher. Strictly speaking, these percentages are by volume, but the errors of reading the result, and those due to solubility of the non-aldehydes in the aqueous liquid render any correction for the specific gravity of the constituents unnecessary in practice. Care must be taken that every particle of the aldehyde compound is dissolved, as otherwise the reading of the oily layer will be obscured, and a serious error may be introduced. If the precipitate does not dissolve after standing 8 hours in the water bath with repeated shaking, the presence of solid resin may be inferred, and the estimation of the aldehyde in this way, with anything like accuracy, is then impossible.

Hirschsohn recommends shaking the oil in a graduated tube with 3 times its volume of light petroleum ether. A diminution in volume of the oil indicates petroleum, resin, or fatty oils (except castor oil). An increase in volume of the oil indicates castor oil. The petroleum layer is then shaken with copper hydroxide. A blue solution indicates copaiba or resin.

This oil is an article of great commercial importance, and finds a very extensive employment in perfumery. Its odour closely resembles that of cinnamon, but it lacks the delicacy of the latter, to which it is often fraudulently added. Pure cinnamic aldehyde or "synthetic cassia oil" is now an article of commerce. It is readily formed by the action of sodium ethylate on a mixture of benzoic and acetic aldehydes. Whilst it possesses the characteristic *cassia* odour to a marked extent, there is nothing else present to in any way modify that odour, in the way that the other constituents of cassia oil do. It may be described as having a stronger but cruder odour, than the natural oil. An objection to some of the commercial aldehyde is that it contains traces of chlorine compounds, introduced during manufacture, which materially depreciate its odour value. Chlorine free cinnamic aldehyde can, however, now be easily obtained. Its value is very similar to that of pure cassia oil of good quality.

Cinnamon Oil.—The cinnamon oil of commerce is understood as the product of distillation of the bark of *Cinnamomum zeylanicum*, the Ceylon cinnamon, a native of this island. The leaves and root bark also yield essential oils, the former of which is of considerable importance commercially. The cinnamon tree is a small evergreen tree with shining leaves and panicles of greenish flowers, of somewhat unpleasant odour. It is extensively cultivated in Ceylon, from which nearly all the bark of commerce is

obtained. It is also grown in India, Mauritius, the Seychelles and Jamaica, but *Ceylon is responsible for practically the* whole of the cinnamon used. Several varieties are cultivated, but whether they are merely the same plant slightly modified by the influence of soil, etc., or not, is uncertain. The south-west of the island in the Colombo, Negumbo and Matura districts produce the majority of the bark, and the famous "cinnamon gardens" of Colombo, which the author recently visited, form one of the great attractions to the island. The age of the tree, the care devoted to its cultivation, and the time at which the bark is gathered largely determine the value of the product. The appearance and size of the "quills," together with their odour and flavour, determine their value on the market. The small fragments or chips and the bark of inferior quality are used in Ceylon for distillation, and also form the chief material from which the oil is distilled in England. The oil distilled in Ceylon is usually obtained by macerating the fragments of bark in sea-water or strong brine for two or three days and then subjecting them to distillation. The yield is from ·5 to 1 per cent. The majority of that exported, however, is not genuine. Either the leaves are added to the bark when distilled, or cinnamon leaf oil is added to the oil after distillation. The important difference between the two oils is that the bark oil owes its characteristic odour to the cinnamic aldehyde it contains, whilst the leaf oil contains only traces of that body; the chief constituent of the latter oil is eugenol, the characteristic phenol of the oils of cloves and pimento.

The more delicate odour of cinnamon oil causes it to be preferred to cassia oil in England, whilst the stronger and coarser odour of the latter, together with its much lower price, gains for it preference in many parts of the continent. Cinnamon oil is worth eight to ten times as much as cassia oil.

The pure bark oil has a specific gravity of 1·025 to 1·035,

rarely exceeding this, though Schimmel & Co. state that they have distilled an oil which had a specific gravity 1·038. Adulteration with the leaf oil or with clove oil increases this figure. The oil is optically inactive, or at most laevo-rotary to the extent of $-1°$. The ascertained constituents are the terpene phellandrene, cinnamic aldehyde, and eugenol. The cinnamic aldehyde is estimated as described under *Cassia Oil*, and should never be less than 50 per cent. The *British Pharmacopœia*, in which this oil is official, gives the following limits: specific gravity, 1·025 to 1·035; cinnamic aldehyde at least 50 per cent.; should not yield a decided blue colouration with ferric chloride solution. Adulteration with much leaf oil causes the characteristic blue colour given by eugenol and ferric chloride to be developed. The amount of eugenol estimated as described under oil of cloves, should not exceed 8 per cent.

Cinnamon leaf oil is also largely used for perfumery and other purposes. The yield is from 1·5 to 2 per cent. of a slightly optically active oil of specific gravity 1·045 to 1·060. It was examined in 1855 by Stenhouse, who stated that it consisted chiefly of eugenol (eugenic acid) and a hydrocarbon, with traces of benzoic acid. Weber (*Arch. Pharm.*, ccxxx., 232) confirmed these results in general, but could find no trace of benzoic acid. A very small quantity of cinnamic aldehyde was, however, found. The content of eugenol is usually from 75 to 85 per cent.

The root oil has been stated to contain eugenol, safrol, benzaldehyde and benzoic esters, but the authenticity of the sample examined is doubtful. The inhabitants of Ceylon obtain from the roots a camphor-like mass, which is made into candles and burnt at festivals. Probably the chief constituent of true root oil is camphor.

Sassafras Oil.—The ordinary oil of sassafras is distilled from the root of *Sassafras officinale* (*Laurus sassafras* of

Linnæus), a native of North America. This tree is one of the most widely distributed in the continent, being found in Canada, in all the States east of the prairies beyond the Mississippi, and in Mexico. In Canada it seldom exceeds 30 feet in height, but in the south, especially in Virginia and the Carolinas, it reaches nearly 100 feet in height. The root bark (except the outer layers) is the most aromatic portion of the plant, and from this, as well as the wood, the essential oil is distilled. The roots may be dug out at any season, but those dug when the sap is not rising yield the highest percentage of oil. Some of the large roots weigh nearly half a ton, but the smaller roots are most valued on account of their higher yield of oil. The typical distilleries in the neighbourhood of Baltimore use wooden tanks as stills. These are made of kiln-dried pine, and consist of wooden boxes built up of staves, with a pierced false bottom. The head is provided with a trap-door for filling by, and a large door is fitted to the bottom of the tank, for the purposes of emptying. To the upper part of the tank is fitted a copper head, leading to a condensing coil immersed in cold water. Steam at from 40 to 60 lb. pressure is admitted between the true and false bottoms. The stream of condensed products issuing from the pipe is caught in a copper funnel with a very long spout which reaches nearly to the bottom of a 20-gallon copper vessel. The oil being heavier than water collects at the bottom, leaving the water to flow away at the top of the vessel. A charge of 10 tons requires about two days to exhaust, and yields about 10 gallons of oil. In parts of Pennsylvania and New Jersey a number of small isolated distillers, often coloured men, carry on a remunerative business in this oil. A most primitive still is used, consisting merely of a barrel with its head luted on, and its bottom pierced and standing on a steam generator. A natural elbow-shaped branch perforated throughout serves to carry the

distillation products to a metal tube placed in a trough of running water. The condensed products are then separated in the usual way. Although the yield of oil is much lower than when distillation is effected in modern apparatus, the process is a payable one, as the capital necessary for such primitive distilleries is very small. Properly treated, as much as 8 per cent. of oil can be obtained from the root bark. Two samples of oil, one from the root bark and one from the wood, were distilled by Schimmel & Co., and had the following characteristics:—

	Yield.	*Specific Gravity.*	*Rotation.*
Bark . .	7·4 per cent.	1·075	+ 3° 16′
Wood . .	·9 ,,	1·075	—

The limits allowable are 1·065 to 1·095 for specific gravity, and + 1° to + 4° for the optical rotation. The earliest chemical investigation of the oil was by Grimaux (*Comptes Rendus*, 1869, p. 928), who stated that it consisted of 90 per cent. safrol (*q.v.*) and 10 per cent. of a terpene which he termed safrene, with traces of a phenol, which was afterwards identified as eugenol. A recent investigation in Schimmel's laboratory has shown that "safrene" is a mixture of the terpenes pinene and phellandrene: dextro-camphor was also found, and a body which was probably cadinene. The average composition of the oil is:—

Safrol	80 per cent.
Pinene	10 ,, (Pinene and Phellandrene together)
Phellandrene . . .	
Dextro-camphor . .	7 ,,
Eugenol	0·5 ,,
Cadinene (?) . . .	2·5 ,,

This oil is used on an enormous scale for soap perfumery. Its strong odour and low price enable it to be used for the very cheapest of soaps, not only to give them an actual perfume, but also to cover up the bad odour of poor quality fats. But its use has been very largely diminished by the

discovery that its active constituent exists in notable quantity in crude camphor oil. By means of fractional distillation and freezing (safrol melts at about 8°), this body can be extracted in a state of almost absolute purity as a water-white liquid of specific gravity over 1·100. In this form it is, in the author's opinion, preferable in every way for cheap perfumery to the natural oil of sassafras, and its manufacture is now an enormous industry. There are many samples, however, on the market of so-called "artificial sassafras oil" which are merely fractionated camphor oil, of specific gravity under 1·000. It should be remembered that these often contain not more than 50 per cent. of safrol, and are far less valuable than the pure safrol. This body can, of course, be frozen out from ordinary sassafras oil, but it is much cheaper to obtain it from camphor oil. Safrol, which is identical with "shikimol" from oil of *Ilicium religiosum*, also finds an extensive use in the manufacture of heliotropine (piperonal), which is one of its oxidation products.

Sassafras leaves also yield a small quantity (·03 per cent.) of an essential oil, differing entirely from the oil from the wood. This has been investigated in Schimmel's laboratory. The oil obtained from 8000 lb. of leaves was only about 2½ lb., and was of a light yellow colour and agreeable lemon odour. Its specific gravity was ·872, and its optical rotation + 6° 25′. The constituents identified were citral, pinene, phellandrene, a hydrocarbon of the paraffin series, a hydrocarbon also found in oil of bay and called by the discoverers myrcene, and the acetic and valerianic (isovalerianic?) esters of linalol and probably of geraniol, and, possibly, cadinene. No safrol could be detected.

Camphor Oil.—Ordinary camphor oil is a by-product in the manufacture of the ordinary or "Japan" camphor. The tree yielding this is perhaps best known as *Camphora officinalis*, but it has been known under several other names,

such as *Cinnamomum camphora* and *Laurus camphora*. The tree is distributed throughout the eastern provinces of Central China, on the island of Hainan, and to a very great extent in Formosa. The Japanese islands Kinshû and Shikoku also produce it very abundantly. According to Yoshida, the older trees contain more camphor than the young ones, and those over a hundred years of age are exceedingly rich. The importance of a regular supply of both camphor and camphor oil is enormous, and the utter neglect which the Chinese gatherers have shown to the cultivation of the tree is very surprising. They have largely succeeded in exterminating it along the seaboard of Formosa, and are continually making fresh inroads into the inland forests, without any serious attempt to replace the trees destroyed. The crude method of preparing camphor from the trees is as follows. The tree is felled and the young branches and twigs are chopped up and packed in perforated jars, and heated over a crude steam bath. The steam enters the jars, saturates the chips, and causes the crude camphor to sublime and condense in earthenware pots placed over the jars. The crude camphor is sent to the port, and a certain amount of oil exudes from it which is collected and is known as oil of camphor. The majority of the oil is, however, produced by distilling the chips with water in crude stills. The crude product amounts to about 3 per cent. of the wood used. The oil is drained from the crystalline camphor, of which it retains a considerable amount in solution. This is transferred to a still, and about $\frac{2}{3}$ is distilled off, leaving the bulk of the camphor in the residue, which is cooled and pressed to separate more camphor. This process is repeated so long as it pays, and the residue forms the camphor oil of commerce. From a scientific point of view, one must regard the whole of the products of distillation of the wood as camphor oil. This, however, contains so much solid camphor, or stearoptene, that it is commercially

regarded as a separate product, and the liquid portion of the oil is thus known as oil of camphor. Hence the great variability in its properties and composition.

The crude camphor arrives in England in a very impure state, and is refined by sublimation, generally with quicklime and charcoal. For details of the process adopted the reader is referred to Pereira's *Materia Medica*, vol. ii., pt. i., p. 450, and Sawyer's *Odorographia*, pt. i., p. 339, where useful accounts are given. The camphor tree is also being successfully cultivated in Florida (see Brannt, *Animal and Vegetable Fats and Oils*, vol. ii., pp. 412, 413). Formerly camphor oil was regarded as having no value. To-day, however, it is used to an enormous extent in the preparation of safrol (see *Oil of Sassafras*). The earliest scientific investigation of this oil was by Beckett and Wright (*Journ. Chem. Soc.*, 1876, p. 7), but the only conclusions they came to were that it was a complex mixture probably containing a hydrocarbon of the terpene series, a body having the composition $C_{10}H_{18}O$, a liquid containing less hydrogen than camphor, and much ordinary camphor. Oishi (*Chem. News*, l., p. 275) described it as a crude oil, of specific gravity ·959, which yielded about 25 per cent. of camphor. The rectified oil was a colourless liquid of specific gravity ·895. He concluded that the oil was a mixture of terpenes, camphors, and some of the oxidised hydrocarbons. Yoshida (*Journ. Chem. Soc.*, 1885, p. 782) separated the oil into four chief portions, which appeared to be (1) a terpene (pinene) boiling at 150°; (2) a terpene (limonene) boiling at 172°; (3) camphor; (4) an oxygenated body which he termed camphorogenol. A sample examined by Trimble and Schroeter (*Pharm. Journ.*, xx., p. 145) was separated into ten fractions, each of which the authors claimed to be pure compounds, but which were clearly mixtures in several cases. No less than five terpenes were given, and five oxygenated bodies. Schimmel & Co. have examined the

oil since, and to them is due the discovery of the presence of safrol, which they now manufacture on an enormous scale. They also showed that Yoshida's camphorogenol had no existence. The result of their researches shows that the following bodies are present in the oil: Pinene, phellandrene, camphene (?), dipentene, cineol, camphor, safrol, eugenol, terpineol (?), and cadinene. Fifteen years ago the camphor oil of commerce, according to Schimmel, had a specific gravity 1·100, but owing to the extraction of as much as possible before it is allowed to leave Japan, that found on the market to-day has a specific gravity seldom exceeding ·960.

MacEwan gives ·943 and ·959 as the specific gravity of a Formosa and a Japan oil respectively, which he examined. As by-products in the manufacture, the separated constituents are sold as light and heavy camphor oil according to their specific gravity and boiling point. Of the latter there is not much to be had, as the process of manufacture extracts nearly all the high boiling constituent, safrol, so that the waste product is chiefly light camphor oil. This can be obtained at 30s. per cwt., with a specific gravity up to about ·910. Samples are often found in London under the name of light camphor oil, with a specific gravity as low as ·880 and less, *consisting almost entirely of terpenes*. The *only* use for the latter body is as a solvent for resins, or for cleaning purposes—indeed, as a partial substitute for turpentine. These details show that camphor oil must be bought for what it is worth. No definite standards can be laid down, and only a complete analysis will show the value of a given sample.

Borneo camphor, or borneol, the product of the tree *Dryobanalops camphora*, yields a corresponding oil, of specific gravity about ·900, which consists chiefly of terpenes. It is not, however, a commercial article.

The leaves of the Japan camphor tree also yield an essential

oil. According to Hooper (*Pharm. Journ.* [56], vol. ii., p. 21), the yield is about 1 per cent. of an oil of specific gravity ·9322 and optical rotation + 4° 32′. It contained 10 to 15 per cent. of camphor. Another specimen contained 75 per cent., and had a specific gravity ·9314 and optical rotation + 27°. There seems not to be much difference between this and the ordinary camphor oil. The roots yield an oil of quite similar character. A sample distilled by Schimmel & Co. had a specific gravity ·975, and consisted chiefly of camphor—the liquid portion resembling commercial camphor oil very closely.

Culilaban Oil.—This is distilled from the fruit of *Cinnamomum culilavan*, which yields from 3 to 4 per cent. of the oil. According to Schimmel, the oil has a specific gravity of about 1·050. It is too dark for its optical rotation to be conveniently determined. The constituents found in the oil are eugenol, methyl-eugenol, and a small quantity of some constituent or constituents with a specific gravity lighter than that of water.

Massoi Bark Oil.—This oil is distilled from the bark of *Massoia aromatica*, in which it occurs to the extent of 6 to 8 per cent. Woy, who investigated the oil (*Arch. Pharm.* [3], xxviii., p. 22), states that it contains a considerable quantity of eugenol, with some safrol, a body resembling creosote, and traces of free acetic acid. He also claimed that it contains a terpene not identical with any already known hydrocarbon. Wallach has, however, shown that this body is a mixture of the terpenes pinene and limonene, with, perhaps, some dipentene. The oil is a clear yellow liquid of clove-like odour of specific gravity 1·040 to 1·060.

Kuromoji Oil.—The leaves and young twigs of *Lindera sericea*, one of the Japanese *Laurineæ*, yield the oil known in commerce under this name. It is a dark yellow oil with a strong aromatic and balsamic odour, of specific gravity from ·890 to ·915, usually about ·900, and faintly laevo-rotary.

It has been examined by Kwasnik, who states that it contains *dextro*-limonene, dipentene, inactive terpineol and *laevo*-carvone. The oil, on account of its comparatively low price (about 8s. 6d. per lb.), has recently come into some favour as an aromatic.

Paracoto Bark Oil.—The botanical origin of the tree which yields this oil is not known with certainty, but it appears to be a lauraceous plant growing chiefly in Bolivia. The yield is from 1 to 2 per cent. of an agreeably smelling oil of specific gravity from ·925 to 1·02. It is slightly dextro-rotary, usually about + 5°. An elaborate account of its composition is given by Brannt (*Animal and Vegetable Fats and Oils*, vol. ii., p. 420), but it is extremely doubtful whether any one of the five constituents there mentioned—*viz.*, α-paracotene, β-paracotene, α-paracotol, β-paracotol, γ-paracotol, have any existence. The only well-ascertained constituents, according to Wallach and Reindorff, are methyl-eugenol and the sesquiterpene cadinene. For some interesting notes on the botany of the tree, see Elborne (*Year Book of Pharmacy*, 1893, p. 327).

Persea Oil.—The dried leaves of *Persea gratissima* yield about ·5 per cent. of an oil of specific gravity ·960, and optical activity about + 2°. It contains, amongst other ingredients, methyl-chavicol.

Pichurim Oil.—The cotyledons of *Nectandra Puchury major* and *Nectandra Puchury minor*, two species of *Laurineæ* indigenous to Brazil, yield about ·5 to 1 per cent. of a yellowish-green oil. According to Müller, the oil contains several oxygenated constituents not completely identified. Esters of lauric and valerianic acids are probably present.

Spice Wood Oil.—The various parts of the plant *Laurus benzoin* (*Benzoin odoriferum*), commonly known as spice wood or wild allspice, yield aromatic volatile oils. The plant

is a North American shrub, inhabiting damp, shady woods in localities extending from Canada to Florida. Messrs. Schimmel & Co. (*Report*, October, 1890) state that all parts of the shrub possess pleasant aromatic odours, which, however, are very different from one another. They obtained: (1) From the bark, ·43 per cent. of an oil smelling like wintergreen. Its specific gravity was ·923, and its constituents boiled between 170° and 300°; (2) From the berries, 5 per cent. of an oil of a spicy aromatic odour, of specific gravity ·855, with constituents boiling between 160° and 270°; (3) From the twigs, ·3 per cent. of an oil smelling like camphor and calamus, specific gravity ·925; (4) From the leaves, ·3 per cent. of an oil of pleasant lavender odour, specific gravity ·888.

The oil from the bark appears to consist largely of hydrocarbons, but also to contain about 10 per cent. of methyl salicylate. Morris Jones (*Amer. Journ. Pharm.*, 1873, p. 300) states that it contains a compound of the cinnamic series.

Californian Bay Oil.—The tree yielding this oil is a large forest tree, common on the mountains of California and the Pacific slope, known as the mountain laurel, sassafras laurel, or Californian olive. Botanically, it is *Laurus Californica* (*Oreodaphne Californica*, Nees). Heaney (*Amer. Journ. Pharm.*, 1875, p. 105) states that the yield of oil from the leaves is 4 per cent. He claimed to have found about 35 per cent. of a hydrocarbon and 65 per cent. of an oxygenated body, which he termed *oreodaphnol* in the oil. This body, however, has never received confirmation, and it is very doubtful whether the hydrocarbon he obtained was pure. He assigned to it a specific gravity ·894 and boiling point 175°. Stillman, on the other hand, claims that it contains terpineol and an oxygenated body of the formula $C_8H_{12}O$, which he named umbellol. According to Schimmel, the only well-ascertained constituent is cineol. The oil is a straw-coloured liquid of aromatic taste, of specific gravity from

·930 to ·950. This oil must not be confused with the ordinary bay oil, which is the product of one of the *Myrtaceæ*.

Laurel Oil.—The leaves of the sweet bay, *Laurus nobilis*, yield from 1 to 3 per cent. of an essential oil of specific gravity ·920 to ·930 and optical rotation − 15° to − 18°; the berries also yield an oil closely resembling that of the leaves, but under 1 per cent. is obtained. Both oils contain the terpene pinene and cineol.

Tetranthera Oil.—The fruit of *Tetranthera citrata* yields about 5 per cent. of an aromatic oil of specific gravity usually about ·920, but varying somewhat widely. Its only well-ascertained constituent is citral.

Caparrapi Oil.—This oil is yielded by the so-called "canelo" tree of Colombia, *Nectandra caparrapi*. It varies in colour from pale yellow to dark brownish red, and is known in commerce under the name of "white" and "black". It is a thick liquid of specific gravity about ·915 to ·935, and rotary power − 3°. On exposure to prolonged cold, crystals of an acid are deposited. The black oil probably owes its colour to overheating. From a sample of the white oil, Tapia (*Bull. Soc. Chim.*, 1898, 638) has extracted an acid of the formula $C_{15}H_{26}O_3$, which crystallises in white needles, melts at 84·5°, and has a rotary power $[\alpha]_d = + 3°$. In addition to this body the oil contains a sesquiterpene alcohol, $C_{15}H_{26}O$, which the same chemist terms caparrapiol. It has a specific gravity ·9146, and a rotary power $[\alpha]_d = - 18·6°$, and boils at 260° at atmospheric pressure. By abstracting water by means of dehydrating agents, a sesquiterpene $C_{15}H_{24}$ is formed, termed caparrapene. This is described as a colourless liquid, boiling at 240° to 250°, and of specific gravity ·9019 and a rotary power $[\alpha]_d = - 2·2°$. These compounds require further examination before they can be regarded as new compounds. The oil is used for the same purposes as balsam of copaiba.

N. O. Myristiceæ.

There is only one genus of this natural order yielding essential oils that are at all well known. This is the genus *Myristica*, the fruit of which consists of the well-known nutmeg enclosed in a shell, which is covered by an arillus (according to Planchon, this latter is only an extension of the exostome, and therefore a false arillus, or arillode). The arillus is known as mace, and from both this and from the nutmeg essential oils are distilled. For a most exhaustive and thorough treatment of the nutmeg and its products, there is no work to equal that recently published in Berlin by Dr. Warburg on *The Nutmeg: its History, Botany, Cultivation, Commerce and Use*, to which the reader is referred for detailed information. For the present purpose, the following details will suffice:—

This natural order is confined to the tropics, and *Myristica fragrans* is the typical plant yielding the ordinary nutmeg. It is an inhabitant of the Moluccas, being specially abundant in the Banda Isles, three of which, Lontar, Pulo Ai, and Pulo Nera, are often known as the "Nutmeg Islands". At one time the Dutch attempted to confine the cultivation to these islands, and when supplies were rather more abundant than usual the excess was said to have been burned in order to keep up prices. The seed was however conveyed elsewhere by the "nutmeg bird," who in swallowing the fruit digested the mace, but voided the nutmeg uninjured. The tree has been successfully introduced into numerous other places, for example, Java, Penang, Bourbon, Zanzibar, and Singapore. A useful description of the cultivation of the tree will be found in the *Journal of the Indian Archipelago*, v., p. 78. Nutmegs are often imported limed, *i.e.*, treated externally with lime, with the object of preventing their germination and keeping them protected from insects. Although quite

unnecessary, this practice is approved of in certain markets, so much so that Penang nutmegs, the most valued in the London market, which are imported unlimed, are frequently limed in London for re-exportation. The nutmegs of other species are often used, both as nuts, mace, and oil, as a substituent or adulteration of the ordinary product. Amongst these are the Malabar nutmegs (from *M. Malabarica*) and New Guinea nutmegs (from *M. Argentea*).

Nutmeg Oil.—Nutmegs yield from 8 to 15 per cent. of volatile oil on distillation. The *British Pharmacopœia*, in which this oil is official, allows to it a specific gravity ·870 to ·910, but in the author's opinion these limits should be rather wider—from ·868 to ·915. It also states that it should leave no crystalline residue on evaporation in a water bath. This is to guard against the presence of traces of the fixed or fatty oil existing in nutmegs, which is carried over mechanically during the distillation. The presence of traces of the fatty oil is said to be objectionable when the oil is used for the flavouring of *sal volatile* (aromatic spirits of ammonia). It may be detected by evaporating the oil, and purifying the crystals by washing them several times with cold alcohol and recrystallising from boiling alcohol. The resulting *myristic acid* melts at 54° to 55°. The oil should be dextro-rotary from + 14° to + 30°, and should be soluble in an equal volume of 95 per cent. alcohol. The chemistry of this oil requires clearing up, as there are many contradictory statements in connection with it. The earlier researches of Schacht (1862), Cloez (1864), and Koller (1865) are by no means in agreement. Gladstone (1872) claimed to have discovered a body boiling at about 212°, to which he assigned the formula $C_{10}H_{14}O$ and named myristicol. Wright (1873) states that the chief constituents were two terpenes and some cymene, besides a high boiling oil of the formula $C_{10}H_{13}O_2$, and a non-volatile resin of the formula $C_{40}H_{56}O_5$. On the other hand, Semmler

(*Berichte*, 1890, p. 1803) has examined the oil and states that he can find no cymene, no myristicol, and no high boiling constituent of the character above referred to. In support of these statements, he also adduces the evidence of several combustions and a molecular weight determination. These results show that the carbon and hydrogen in the oil amount to over 99·5 per cent., and the molecular weight determination (vapour-density determination) gave 138 as against a theoretical 136 for terpenes. Hence Semmler concludes that the oil consists almost entirely of terpenes. It must be noted, however, that the oil upon which Semmler worked had a specific gravity ·8611 and was not prepared by himself. Hence, although its purity appears unquestionable, it is probable that it had been rectified and the high boiling constituents got rid of, for ordinary commercial oils always possess a higher specific gravity than this. The statement occurring in Sawyer's *Odorographia*, that Semmler discovered myristicin in oil of nutmegs, is not correct.

Mace Oil.—Much of the mace oil of commerce is merely nutmeg oil, distilled from poor quality nutmegs. The true mace oil is much more expensive and has different characters to nutmeg oil. Its specific gravity varies between ·910 and ·932, and its optical rotation is about + 10°. The yield of oil is from 4 to 15. Some of the mace of commerce has been extracted with alcohol before being imported, hence its low yield of essential oil. With regard to the chemistry of this oil, Wallach identified in it *dextro-* and *laevo*-pinene and dipentene. Semmler (*Berichte*, 1890, p. 1805) confirms the presence of about 50 per cent. of terpenes. About 15 per cent. distilled between 70° and 114° at 10 mm. pressure and appeared to contain myristicol, $C_{10}H_{16}O$. The higher boiling portion contained a phenol and a crystalline compound forming white needles melting at 30°, to which the investigator assigned the formula $C_{12}H_{14}O_3$ and the name

myristicin. This name is unfortunate, as it is in no way related to the glyceride of myristic acid, known under the same name and occurring in the fixed oil of nutmeg. Semmler's myristicin is, chemically, *oxymethylene-methoxy-butenylbenzene* of the constitution—

$$\begin{array}{c} O \\ CH_2 \qquad C_6H_2(OCH_3) . C_4H_7, \\ O \end{array}$$

thus occupying a position between piperonic and apionic aldehydes.

N. O. Euphorbiaceæ.

Cascarilla Oil.—The bark of *Croton elutheria*, a native of the Bahamas, usually known as cascarilla bark, yields from 1 to 3 per cent. of an aromatic oil. It is a light brown liquid of specific gravity ·890 to ·930, and dextro-rotary to the extent of + 5°. Little is known of the chemistry of the oil, but it probably contains at least one terpene and one oxygenated body. Its use is very limited in the preparation of certain perfumes and cordials. The bark itself is very aromatic, and when burned gives off sweet smelling vapours, which accounts for its frequent employment in the manufacture of fumigating pastilles.

N. O. Cupuliferæ.

The only oil of importance yielded by this natural order is that from the bark of *Betula lenta*, the sweet birch, but as this is almost identical with, and usually substituted for, that from *Gaultheria procumbens*, one of the Ericaceæ, it will be more conveniently described with the latter (*q.v.*).

N. O. Santalaceæ.

Santal-wood Oil.—The chief santal-wood oil of commerce, which is largely employed in medicine and perfumery, is the

product of distillation of the wood of *Santalum album*. This oil is known as East Indian santal-wood oil. Probably the Macassar oil is the product of the same tree. *Santalum album* is a native of the mountainous parts of India, but is especially found in Mysore, Malabar, and Coimbatore. It likewise grows on the Coromandel coast, in Madura and Assam. In the Madras presidency and Mysore it is now grown on Government plantations from seeds; experiments in this direction have been carried out in West Australia (which yields another species of santal), but hitherto without success. The wood is sold at the Government auctions, and the latest classification—for the various woods are not of equal value—with which the billets are marked is as follows:—

1. *First Class Billets* (or *Vilayat Budh*). Consists of thoroughly sound billets weighing not less than 20 lb., and not exceeding 112 pieces to the ton.
2. *Second Class Billets* (or *China Budh*). Consists of slightly inferior billets weighing not less than 10 lb., and not exceeding 224 pieces to the ton.
3. *Third Class Billets* (or *Panjam*). Consists of billets having small knots, cracks and hollows, weighing not less than 5 lb., and not exceeding 448 pieces to the ton.
4. *Chotla* (or billets of short length). Consists of short sound pieces, no limit as to weight or number.
5. *Chat Badala*. Consists of billets with knots, cracks and small hollows at either end, weighing not less than 10 lb., and not exceeding 240 pieces to the ton.
6. *Bagaradad*. Consists of solid pieces, without limit as regards dimensions, weight or number.

   N.B.—Billets of Classes 5 and 6 are not planed nor are their edges rounded off.

7. *Roots* (First Class). Consists of pieces weighing not less than 15 lb., and not exceeding 150 pieces to the ton.
8. *Roots* (Second Class). Consists of pieces weighing not less than 5 lb., and not exceeding 448 pieces to the ton.
9. *Roots* (Third Class). Consists of small and side roots below 5 lb. in weight.
10. *Jugpokal* (First Class) (or *Badala*). Consists of hollow pieces weighing not less than 7 lb., and not exceeding 320 pieces to the ton.

11. *Jugpokal* (Second Class). Consists of hollow pieces weighing not less than 3 lb.
12. *Ain Bagar.* Consists of solid, cracked and hollow pieces, weighing not less than 1 lb.
13. *Cheria* (or large *Chilta*). Consists of pieces and chips of heartwood weighing not less than ½ lb.
14. *Ain Chilta.* Consists of pieces and small chips of heartwood.
15. *Hatri Chilta.* Consists of heartwood chips and shavings obtained by planing.
16. *Milwa Chilta.* Consists of pieces and chips having in fair proportions heartwood and sapwood.
17. *Basola Bukni.* Consists of small heartwood and sapwood chips.
18. *Sawdust* (or *Powder*). Obtained in sawing the santal-wood.

The yield of oil is very variable, sometimes falling as low as 1½ per cent., sometimes rising to 6 per cent. In order to extract the oil, the wood must be rasped as fine as possible by special machinery and distilled with high pressure steam. The native distillers use an open fire, and naturally obtain a very inferior oil. The oil is largely used in medicine and perfumery, and is official in the *British Pharmacopœia.* It is a pale yellow, sometimes almost colourless, thick oil of characteristic aromatic odour, of specific gravity about ·975 to ·980. The 1885 *Pharmacopœia* gives the figure as ·960, but the 1898 edition has corrected this obvious error and gives ·975 to ·980. The author has met with genuine samples with rather wider limits than these, from ·973 to ·981. The earlier fractions of the distillation have a lower gravity than the later ones, so that unless the process be carried to its extreme limit the oil may have a rather lower gravity than allowed by the *B. P.* This point is illustrated by the following three fractions—the first, middle and last two ounces from a 20 lb. batch of oil, distilled by the late Mr. Conroy for the author :—

First	·9649
Middle	·9758
Last	·9808

The optical rotation of the oil is fairly constant, seldom, if ever, varying outside the limits − 15° to − 20° (the *B. P.*

gives − 16° to − 20°). An important feature in examining the oil is its solubility in from 5 to 6 volumes of 70 per cent. alcohol. Its high boiling point is also characteristic. Under ordinary pressure it undergoes slight decomposition, but at 14 mm. nothing should distil over under 150°, whilst 80 to 90 per cent. of cedar-wood oil, a common adulterant, is obtained below this temperature. An important method of examining the oil is the acetylation process (*q.v.*) first applied by the author to this oil (*Pharm. Jour.*, lv., p. 118). Santal-wood oil requires from ·7 to 1·5 per cent. of potassium hydroxide to saponify the esters present. After acetylation, however, the oil requires about 20 to 21 per cent. of KOH to saponify it, thus indicating the presence of a large quantity of alcoholic constituents. The details of this process, and the calculations required, have been given on page 92. The free alcohols are usually calculated as santalol $C_{15}H_{26}O$, and should never fall below 90 per cent. Cedar-wood oil, gurjun oil, and copaiba oil all yield a very low acetylation figure (calculated as santalol, as follows: cedar oil, 8 to 12 per cent.; copaiba oil, 5 to 8 per cent.; gurjun oil, 7 to 10 per cent.). Castor oil is also sometimes added as an adulterant, but is easily detected on account of its lower gravity and high saponification number.

Chapoteaut examined this oil (*Bull. Soc. Chim.*, xxxvii., p. 303) and stated that it contained the aldehyde santalal $C_{15}H_{24}O$ and the alcohol santalol $C_{15}H_{26}O$, the former being in excess. But as the oil upon which he worked had a specific gravity ·945, his results are not reliable. The author's experience, amply confirmed by Umney, Schimmel, Dulière and others, is that the alcoholic constituent or constituents largely predominate. Chapman (*Proc. Chem. Soc.*, clxiv., p. 140) claims to have isolated santalal $C_{15}H_{24}O$ as a liquid of specific gravity ·9793 and specific rotation − 14° 42′, but no proofs of its purity are adduced. Santalol is now an article of commerce.

A sample prepared by Schimmel & Co., and examined by the author, had a specific gravity ·979 and an optical rotation − 18°. The author has repeatedly expressed the opinion that "santalol" is not a pure compound, but a mixture of more than one alcohol. This opinion has recently been confirmed by Schimmel & Co., who give the following details of their examination of samples of this body (*Report*, April, 1899, p. 38).

East Indian sandal-wood oil consists of 94 to 98 per cent. of alcoholic constituents, commonly called santalol. This is obtained by saponifying the oil and by subsequently rectifying it by distillation under low pressure or with overheated steam. A recent comparative examination of several samples gave the following results:—

Sample.	*Specific Gravity.*	*Saponification Figure (°/₀ KOH).*	*Boiling Point 11 mm. pressure.*	*Percentage of Santalol calculated for $C_{15}H_{26}O$.*
1	·979	·13	168° to 169°	98·8
2	·980	·63	—	100·3
3	·979	·80	168° to 170°	99·3
4	·979	·35	—	100·1

As is to be seen from these figures, the saponification in no case has been complete. In order to prepare pure santalol we proceeded in the following way: 100 gm. of East Indian sandal-wood oil of specific gravity ·977 and saponification figure ·44 and containing 94·1 per cent. of santalol were heated to 80° with an equal weight each of phthalic anhydride and benzene upon a water bath for one hour; the acid esters formed were combined with alkali and dissolved in an excess of water. The aqueous solution was deprived of the non-alcoholic constituents by agitation with ether, repeated three times, and the acid esters were separated by the addition of dilute sulphuric acid; subsequently they were saponified by means of alcoholic solution of potassium hydroxide, and the santalol set free was deprived of adhering

alkali and alcohol, by washing it with water. By fractionating under 13 mm. pressure the following fractions were obtained :—

1.	170° to 172°;	sp. gr. ·978;	opt. rot. − 15° 22′
2.	172° „ 172°;	„ „ ·979;	„ „ − 18° 0′
3.	172° „ 172°;	„ „ ·979;	„ „ − 26° 47′

None of these fractions gave a figure of saponification. The product obtained amounted to 85 per cent. of the oil used. The odour slightly resembles that of sandal-wood oil. Although this product may be devoid of esters and other "non-alcoholic" constituents, it can by no means be considered a definite chemical compound, for the reason that its optical rotation reveals too considerable differences between the three fractions.

In order to settle this point, fraction 1 was furthermore submitted to fractional distillation and a substance obtained which boiled at 165° and 167° under 13 mm. pressure, and had the specific gravity ·970 and optical rotation − 7° 20′. Treated in the same way, fraction 3 rendered a product having a considerably higher boiling point, namely, 173° under 13 mm. pressure, specific gravity ·979 and optical rotation − 32° 36′. A substance yielding upon fractionation two products so much differing cannot be considered an individual chemical compound. Santalol, therefore, is a mixture of two sesquiterpene alcohols of which the one with a lower boiling point seems to be optically inactive or possibly dextro-rotary, while the other having a higher boiling point is strongly laevo-rotary. Further researches will lead to the determination of the chemical composition and the properties of these alcohols.

It is remarkable that the esters contained in East Indian sandal-wood oil have a lower boiling point (132° to 164° under 11 mm. pressure) than the sesquiterpene alcohols. To all appearances they contain other alcoholic constituents than the santal alcohols.

It may also be stated that santalylphthalic acid could not be made to crystallise, even after it had been kept at a low temperature for weeks. Santalylphthalate of silver melts at about 50°, and is difficult to be recrystallised.

The author is now engaged in further investigating this interesting oil. West Australian santal-wood oil is the product of another species of santal, being chiefly if not entirely derived from the wood of *Santalum cygnorum*. Several other species are found in West Australia, but they are much less common than *Santalum cygnorum*, which alone is used to any extent for distilling. Although only a tree of small dimensions, it forms an important factor in the timber industry of Western Australia. The species, as the author has seen it growing in the interior of this colony, has a low depressed habit, and is usually very branchy and heavily topped. It is generally from 12 to 20 feet high, and from 6 to 10 inches in diameter. The stems usually weigh from 1 to 6 cwt. It is found fairly well distributed in the interior of the colony, except in the extreme south-west. It may be seen growing fairly freely on the most barren sandy soil, where one could not see a blade of grass nor a drop of water for miles round. The greater part of this wood is exported to China, but one or two santal oil distilleries have been started in the colony. The author has examined four samples of oil distilled from either *Santalum cygnorum*, or, from this tree with other species mixed (for there are several closely allied species growing in Western Australia), for which he is indebted to the kindness of Mr. Samuel Lambert, and found they had the following characteristics :—

	Specific Gravity.	*KOH for Esters.*	*Iodine Absorption.*
1 . .	·9650	1·46	200·0
2 . .	·9644	1·15	204·5
3 . .	·9632	1·66	198·2
4 . .	·9643	1·35	197·6

There was found only about 75 per cent. of santalol in these oils, as against 90 per cent. in the East Indian oil.

In South Australia *Santalum preissianum* is used for distillation, but it yields an oil quite different to the ordinary santal-wood oil. It has a specific gravity of about 1·02, and becomes solid when cooled.

Berkenheim has isolated from this oil a solid alcoholic constituent of the formula $C_{15}H_{24}O$, melting at 101° to 102°, and yielding crystalline esters (*Journ. Chem. Soc.*, 1893, ii., 666).

The so-called West Indian santal-wood oil is the product of a Venezuelan tree which has been identified as belonging to the N. O. Rutaceæ, but as the oil is allied so closely to the true santal-wood oils, it may be conveniently described here. Its specific gravity is lower than that of the true santal oil, and it is far more insoluble in alcohol. It is *dexto*-rotary and contains much less alcoholic constituents than does the oil of *Santalum album*. Five samples gave the following figures:—

	Specific Gravity.	*Solubility in 70 per cent. Alcohol.*	*Rotation.*	*Alcohols as Santalol.*
				Per cent.
1	·962	1 in 80	—	42
2	·966	1 in 55	+ 25° 30′	50·5
3	·953	Insoluble in 80	+ 8°	30·1
4	·963	Insoluble in 80	+ 30° 20′	32·1
5	·962	Insoluble in 80	+ 25° 75′	—

Mr. E. M. Holmes has recently examined the plant yielding this oil, and named it *Schimmelia oleifera* after the well-known Leipzig firm who obtained the specimens for him, but Urban has now proved definitely that the plant belongs to the genus *Amyris*, and has identified it as *Amyris balsamifera*.

African santal-wood oil is the product of a tree of unknown origin. The oil has a specific gravity of about ·965. It appears

to resemble West Indian oil somewhat, but requires further examination. Fiji santal-wood oil is the product of the wood of *Santalum Yasi*. Umney obtained 6¼ per cent. of oil from this wood, with a specific gravity, according to MacEwan, ·9768. It is laevo-rotary − 25° 50′.

The comparative values of the commercial santal-wood oils are approximately as follows:—

East Indian Oil, 15s.	West Indian Oil, 6s. to 7s.
West Australian Oil, 8s. to 12s.	African Oil, 5s. to 6s.
Macassar Oil, 11s. to 12s.	

N. O. ARISTOLOCHIEÆ.

The oils produced by this family of plants are not of much importance, and are but few in number so far as is at present known.

Asarum Oil.—The ordinary European snake-wood oil is distilled from the root of *Asarum europaeum*, which yields about 1 per cent. of a thick, dark brown oil of sweet aromatic odour. The specific gravity of this oil varies from 1·05 to 1·07. According to Petersen, when frozen it deposits crystals of asarol (*q.v.*). It also contains pinene and methyl-eugenol, and possibly methyl-*iso*-eugenol. The whole plant has been subjected to distillation by Zeller, who obtained about ·2 per cent. of an oil which is stated not to contain asarol at all.

Canadian Snake-root Oil is the corresponding product from the root of *Asarum canadense*. The yield is from 3 to 5 per cent. of an oil of strong aromatic odour, specific gravity ·930 to ·960. According to Power, this oil contains a terpene, which he called asarene, but which is probably pinene, asarol and its acetic and valerianic esters. It also contains a little methyl-eugenol. Petersen has confirmed the presence of pinene in this oil.

Virginian Snake-root Oil is the product of distilla-

tion of the whole herb *Aristolochia serpentaria.* It is an oil of specific gravity about ·990, and, according to Schimmel, contains borneol. It possesses an odour recalling valerian and camphor. The root of *Aristolochia clematitis* also yields an oil of specific gravity about ·910, but its composition is not well known.

(B) *Gamopetalæ.*

N. O. LABIATÆ.

Few natural orders yield so many essential oils of great commercial value as does this. Amongst the more important of these are lavender, peppermint, rosemary, patchouli, pennyroyal, spike and thyme oils. Several of these are amongst the best illustrations of the great effects of climate and soil on the essential oils of the same plant grown under different conditions.

Lavender Oil.—This oil is obtained by distilling the flowers of *Lavandula vera*, the well-known lavender, a native of Southern Europe. The plant is found on the stony declivities of the Provencal Alps, the lower Alps of Dauphiné and Cevennes (and even so far north as latitude 46°), in Piedmont, Switzerland, the mountains of Liguria and Etruria, and various other places. Peculiarly enough, the plants come to their greatest perfection and yield a much finer essential oil when transferred from their native soil, and carefully cultivated in certain districts in England, which produces the finest lavender oil in the world. The principal lavender plantations in England are in the neighbourhoods of Mitcham, Ampthill, Hitchin and Canterbury.

Attempts have been made to establish plantations in Southern France from young plants taken from parent stems in England; but the plants quickly reverted to their original condition, and "English" lavender oil can so far only be

produced in England. For the details of the methods of cultivation adopted, the reader is referred to the excellent monograph in Sawyer's *Odorographia*, vol. i., p. 361. A great deal of the finest lavender oil is distilled with water over an open fire, and, so long as care is taken that the plants themselves are not burnt, the fine quality of the resulting oil largely justifies the process. In England it is usual to allow the body of the still in which the flowers are distilled to be very shallow as compared with its width, in order to allow the oil to pass over rapidly and get away from the source of heat, which might damage its odour. If a naked fire be used, it is customary to suspend the charge of flowers in a basket of sheet copper, with perforations all over it to allow the free circulation of water. This basket, of course, holds a large charge, and is manipulated by means of a pulley or swing-crane. The basket should be about an inch from the bottom and sides of the still, and have copper legs to rest upon. Sufficient water is used with each charge to cover the top of the basket. The finest portion of the oil condenses during the first half-hour to hour of the distillation, and is usually reserved, the remainder being collected separately. Rectification of lavender oil, which renders it colourless, does not improve it. The somewhat "herby" odour of the fresh oil soon passes off, and if the oil be kept in cool dark places it improves by maturing for several years, and matured oils are often sold according to the date of their preparation. After a certain time it is said to deteriorate unless a little alcohol is added to it.

The chief difference between English and French oils of lavender lies in the fact that the former only contains about 7 to 10 per cent. of esters calculated as linalyl acetate, whereas the latter contains up to 40 per cent. and over. Messrs. Schimmel have actively endeavoured to establish this ester content as the basis of the valuation of the oil. They main-

tain the superiority of fine French oil over English oil, and go so far as to say that the latter cannot compete with the former. The author, in common with most others, holds the opposite opinion, and considers that no comparison can be made between the two oils on the basis of their ester content. This is much accentuated, if such were necessary, by the fact that linalyl acetate is not *the* odoriferous ingredient of oil of lavender. It is so much modified by the presence of other bodies, as to be regarded as only one of the odoriferous compounds in the oils. Pure linalyl acetate has a marked bergamot odour, and may be regarded as the characteristic ingredient of that oil. The fact that English oil fetches from 6 to 10 times as much as French oil speaks for itself. For a comparison of oils grown in the same locality, the ester comparison may, however, be of service. The oils produced in the south of Europe are finer according as the plants are growing at greater elevations, and according to Schimmel & Co. the very finest oils are produced from the higher valleys of the Savoy Alps, yielding 44 per cent. of ester. The fine oils yielding 38 to 40 per cent. of ester are usually obtained from the Alpes Maritimes and the Basses Alpes, close to the Italian frontier. Less fine, but still excellent oils, with 28 to 32 per cent. of ester are obtained from the French departments of the Gard, Drôme and Hérault.

Lavender oil is a pale yellow oil of specific gravity ·885 to ·900, and optical rotation - 5° to - 10°. The *British Pharmacopœia* requires the specific gravity to be at least ·885, and the oil to be soluble in 3 volumes of 70 per cent. alcohol. With regard to any further tests to be applied to the oil, the place of origin must be taken into consideration. An English oil will not give an ester number outside the limits 7 to 10 per cent., calculated as linalyl acetate, whilst foreign oils yield from 28 to 44 per cent. This fact is ex-

ceedingly important in discriminating between English and mixed lavender oils. The usual adulterants of lavender oil are spike oil and turpentine. Neither of these oils contains appreciable quantities of ester, so that the ester determination affords much information here. Spike oil being slightly dextro-rotary causes a diminution in the rotary power of the oil. American turpentine has the same effect, whereas French turpentine increases the laevo-rotation. Mixtures of spike oil and French lavender oil can be made having the same ester content as English oil, but the optical rotation is interfered with (the specific gravity is slightly raised also, but not necessarily above the limits for normal oil).

Semmler and Tiemann (*Berichte*, xxv., p. 1180) showed that lavender oil contained traces of the terpene limonene, a sesquiterpene, and an alcohol together with its acetic ester, which they called lavendol. Bertram and Walbaum showed that this alcohol was in reality linalol. Schimmel & Co. have detected traces of pinene and of geraniol, the latter probably existing in the form of esters. Hirschsohn has also detected traces of cineol. The chief differences between English oil and French oil are the variations in ester percentage already referred to, and in the fact that English oil contains some quantity of cineol, whereas French oil contains it only in traces (spike oil is also rich in cineol). Duyk states that borneol and its esters occur in the oil, and Bouchardat has found traces of *dextro*-camphene. Traces of a stearoptene are also found. As a favourite perfume lavender oil is second to very few, enormous quantities of the oil being consumed in the popular form of lavender water, and it is in such diluted forms that the delicacy of the odour of the finer oils is so pronounced. The commercial value of French oils is from 5s. to 10s. per lb., according to quality, as against about 50s. for English oil.

Several other species of lavender yield oils that have been superficially examined (in addition to spike oil—which is the product of *Lavandula spica*). The oil from *Lavandula pedunculata* has a specific gravity ·939 and optical rotation - 45°. It contains nearly 40 per cent. of esters, in addition to cineol and possibly thujone. The oil of *Lavandula Stœchas* (the "holy rosemary" of the Spaniards) resembles rosemary rather than lavender in its odour. Its specific gravity is about ·940. The oil of *Lavandula dentata*, of specific gravity ·926, also resembles rosemary, with a marked camphoraceous odour. Charabot (*Bull. Soc. Chim.*, xvii., p. 378) records the examination of a sample of Spanish lavender oil, but does not state its source. He found in it much free linalol, but only 3 per cent. of esters. Borneol was also present.

Spike Oil.—Spike oil, or spike lavender oil, is distilled from the flowering herb *Lavandula spica*, which grows in the same localities as *Lavandula vera*. The yield is from ·5 to 1 per cent. of an oil of much less agreeable odour than that of the true lavender, combining that of the latter plant with that of rosemary.

Pure spike oil is pale yellow to nearly colourless and possesses a specific gravity varying from ·905 to ·918. It is dextro-rotary from + 1° to + 4° and occasionally up to + 7°. It should dissolve in three times its volume of 70 per cent. alcohol, an important test, as very small quantities of the favourite adulterant, turpentine, interfere with its solubility. As spike oil contains a large proportion of free alcohols, it is important to estimate these. Calculated as linalol $C_{10}H_{18}O$, a pure spike oil should yield from 30 to 40 per cent. of alcohols when estimated by the acetylation process. Messrs. Schimmel & Co. propose distilling the first 10 per cent. from the oil and examining its rotary power. Four authentic samples gave the following results:—

Sp. Gravity.	*Rotation of Oil.*	*Rotation of first 10 per cent.*
·916	+ 7° 7′	+ 7° 11′
·915	+ 7° 3′	+ 5° 10′
·914	+ 5°	+ 7° 11′
·918	+ 5° 30′	+ 6° 7′

Adulteration with French turpentine oil to any extent would cause this fraction to be laevo-rotary. In order to ensure uniform results a Ladenburg flask is employed, as illustrated. The lower bulb should hold about 125 c.c., and 5 c.c. should be distilled from 50 c.c. of the oil.

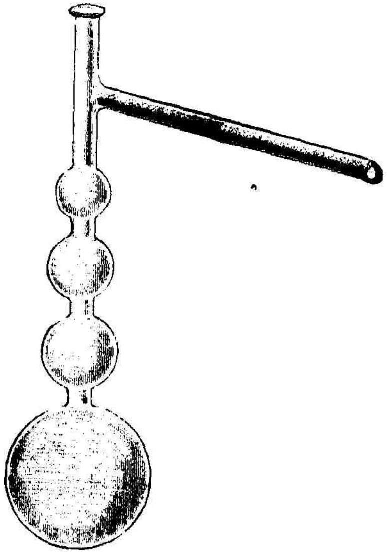


FIG. 15.

In addition to the specific gravity, rotation, rotation of the first 10 per cent. distilled, and estimation of free alcohols, the saponification test should also be applied. Pure spike oil requires practically no potash for saponification, as it is nearly free from esters, in contradistinction to true lavender oil.

Our knowledge of the chemistry of this oil is chiefly due

to Bouchardat, who in 1888 showed that it contained pinene and cineol (eucalyptol). Later, he proved the presence of camphor, linalol, borneol and camphene. Terpineol and geraniol are also present in small quantities. Probably a sesquiterpene also exists in this oil, but its presence has not yet been definitely proved. The similarity of the odour of this oil to true lavender and rosemary is easily explained when one considers that the chief ingredients of the oil are cineol, borneol, linalol and camphor. Linalol is an important ingredient of lavender oil, whereas cineol, borneol and camphor oil are all present in rosemary oil.

Spike oil is largely adulterated with turpentine, and probably, according to Umney, with the commoner varieties of rosemary oil. The former is detected by the alteration in specific gravity and solubility, whilst the latter interferes with the solubility and the percentage of free alcohols present. Spike oil is largely used in cheap perfumery and in the manufacture of certain kinds of lacquer for fine china manufacture. It is also largely employed as an adulterant of ordinary oil of lavender.

Oil of Rosemary.—This oil is distilled from the flowering tops of the plant *Rosmarinus officinalis*, a native of the south of Europe.. The rosemary is a plant largely influenced, as are most of the plants of this natural order, by variations in soil and climate, and the marked differences in English and foreign oils is more than can be explained by care in the method of production. The plant is grown in a few places in England, but the greater part of the commercial oil is produced in the south of France. Other countries on the Mediterranean littoral produce small quantities, but after the south of France the chief source of the oil is the Dalmatian islands. The produce of these islands is chiefly brought into commerce *viâ* Trieste, and this is the oil usually known in trade as Italian rosemary oil. The English oil is by far the

most valued, and commands an infinitely higher price than the foreign oil. The Italian (Dalmatian) oil is the least valuable. In England and the south of France, rosemary is distilled as quickly as possible after it is cut, and in the same manner as lavender flowers. Care is taken to exclude the woody parts of the plant, as not only do these take up unnecessary room in the stills, but also impart an objectionable odour to the oil. The best oil is that which distils over during the first hour of the process. The finest French oil comes from the departments of Gard and Hérault, and the neighbourhood. The supply of oil from the Dalmatian islands is somewhat irregular, and, according to Schimmel & Co., the reason of this is that the rosemary woods, as they are called, are municipal property, and are leased to the peasants and distillers, but with an effective control as to harvesting. This follows a regular rotation, the general crop being gathered in one year and very sparing crops for the next two years. The richest plants grow on the island of Solta, but the successful cultivation of vineyards has nearly replaced the rosemary industry. A little is cultivated on the island of Lissa, but the majority comes from Lesina. The total production of these islands varies from 15,000 to 50,000 pounds per annum. The plants are usually sun-dried before distillation, and the process is carried out in very primitive apparatus, which facts possibly account largely for the inferior quality of the oil. The adulteration practised on this oil appears to commence at Trieste, and not on the islands. The usual adulterants are turpentine and petroleum oils, although the finer qualities are at times adulterated with spike oil. The chief employment of this oil is in perfumery, the well-known *Eau de Cologne* containing oil of rosemary. It has also a limited use in pharmacy, being used, for example, to perfume the official soap liniment, and it is official in the *British Pharmacopœia*. This authority requires that the oil shall

have a specific gravity ·900 to ·915, to be dextro-rotary to + 10°, and to be soluble in two volumes of 90 per cent. alcohol. Cripps (*Ph. Journal*, xxi., p. 937) states that English oil has a specific gravity of ·901 to ·924, whereas foreign oil varies from ·881 to ·907; and that the English oil is laevo-rotary. These observations do not appear to have been carried out altogether on reliable oils, for genuine rosemary oil, whether English or foreign, should never have a specific gravity below ·900. The limits ·900 to ·918 may be regarded as covering all genuine oils, which should be dextro-rotary from + 1° to + 12°. The solubility in alcohol is also important, as the chief adulterants, turpentine and petroleum, are much less soluble than the pure oil. Genuine rosemary oil should dissolve in from ½ to 2 volumes of 90 per cent., and in 10 volumes of 80 per cent. alcohol. The presence of much petroleum oil is also indicated by evaporating the oil in a water bath, when pure rosemary oil should only leave a slight resinous residue, whilst the petroleum (necessarily the higher fractions of petroleum oil, in order not to unduly interfere with the specific gravity) will be left unvolatilised. The addition of alcohol to the oil may be detected by the addition of a crystal of magenta to the oil dried over calcium chloride. The dye is insoluble in the oil, but imparts a pink colour to it if alcohol be present. Fractional distillation, however, with appropriate tests for alcohol to the first distillate, is better.

Schimmel & Co. propose the distillation of the first 10 per cent. of the oil and examination of its rotatory power. Pure oils, they state, invariably yield a dextro-rotary fraction. Five samples distilled by themselves gave the following results :—

	Yield.	*Specific Gravity.*	*Rotation.*	*Rotation of first 10 per cent.*
1 .	1·4 per cent.	·913	+ 4° 16′	+ 1° 30′
2 .	1·7 ,,	·909	+ 3° 40′	+ 1° 22′
3 .	1·5 ,,	·910	+ 5° 54′	+ 6° 26′
4 .	1·73 ,,	·904	+ 6° 54′	+ 7° 49′
5 .	1·78	·906	+ 8° 52′	+ 8° 24′

The estimation of the esters and free alcohols, by saponification and acetylation with a second saponification, yields valuable information. The results are expressed as borneol and bornyl acetate. According to Schimmel & Co., about 6 per cent. of borneol and 17 per cent. to 20 per cent. of bornyl acetate are present. When fractionally distilled not a great deal should come over under 170°. The quantity will naturally vary according to the form of apparatus used, but under no circumstances should more than 15 to 20 per cent. be obtained. Adulteration with turpentine is probable, if as much as this distils over.

According to Haller (*Comptes Rendus*, cviii., p. 1308), the "camphor" of rosemary oil consists of *dextro*-camphor, *laevo*-camphor, *dextro*-borneol and *laevo*-borneol. Esters of borneol are also present, chiefly the acetate. Hirschsohn found cineol in the oil, and Schimmel & Co. have identified the presence of pinene and camphene. The pinene appears to be present, partly at all events, as *dextro*-pinene. The statement of Brannt (*Animal and Vegetable Fats and Oils*, vol. ii., p. 570) that "rosemary oil consists of a *laevo*-terpene (80 per cent.) which may probably be entirely *laevo*-pinene" is entirely erroneous, and evidently based on the examination of adulterated samples.

Peppermint Oil.—This important oil is the product of the distillation of the herbs *Mentha piperita* and *Mentha arvensis*, the latter producing the "Japanese" oil and the former all the other distillates.

Commercially, peppermint oil appears to have commenced its history about 1750, when cultivation was commenced at Mitcham in Surrey. To-day the English peppermint fields are chiefly located in this district, and in the neighbourhoods of Market-Deeping in Lincolnshire, Hitchin in Hertfordshire, and Wisbeach in Cambridgeshire. The oil produced by English-grown plants bears the same relation to most of

the foreign oil, as is the case with lavender oil, although it is claimed that certain distillates of German plants approach the English variety in fineness of odour, as they certainly do in price. Distillation of the oil in America, which is now the most important producer of peppermint oil, commenced in the early part of the present century, when a small distillery was erected in Wayne County, New York State. To-day many thousand acres are under cultivation, and the principal districts producing the oil are Wayne County (New York), various portions of the State of Michigan, especially Wayne County (Michigan), Van Buren, St. Joseph's and Kalamazoo Counties; St. Joseph's County, Indiana; and to a smaller extent in some of the counties of Ohio and in some parts of the south of the Canadian province Ontario. The whole of the peppermint cultivation in America is thus confined to the north-east portion of the United States and extreme south of Canada. In Germany, plantations have been successfully established at Miltitz, in the neighbourhood of Leipzig, by Messrs. Schimmel & Co., and a fine oil is obtained from the plants grown there. A small quantity of oil is also produced in France, in the departments of the Yonne and du Nord. Japan and, to a certain extent, China produce large quantities of peppermint oil. Mr. E. M. Holmes identified the Japanese plant as *Mentha arvensis*, and as the Chinese plant differs slightly from the Japanese, he retains, for the sake of distinction, the names *Mentha arvensis var. piperascens* for the Japanese, and *Mentha arvensis var. glabra* for the Chinese plant. The chief Japanese plantations are located north of Yokohama, and southwards into the provinces of Bingo-Bitchin. The largest centre of cultivation is in the province of Uzen, which produces more oil than all the other provinces put together. Uzen is in the north-east of the island of Hondo, the chief of the Japanese islands. After Uzen, Bingo is the most important producing

province. The following map (reproduced by the courtesy of the editor of the *Chemist and Druggist*) illustrates the chief peppermint districts in Japan :—

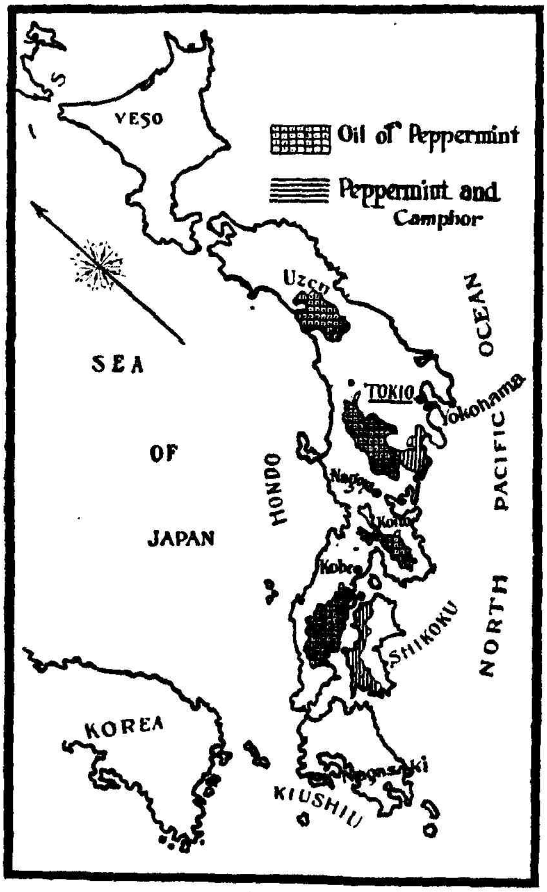


FIG. 16.

In England two varieties of the plant are grown, known as "black" and "white" mint. Of these the former is the coarser plant, rarely flowering in England, and yielding rather more oil of somewhat less delicate aroma than the white

mint. The herbs are distilled in the green state, although sometimes left for a day or two in heaps, after being cut. In England most of the stills used hold from 4 to 8 cwt. of herbs, and have a false bottom which is covered to the depth of two feet with water, and direct heat is then applied. The distillation is carried on for about five hours. The yield varies according to the season from about ½ to 1 per cent.

In America, the mint is usually left in the sun in small cocks for a short time before distillation. With regard to the advisability of drying the plants before distillation, thus reducing the bulk and so increasing the charge of a still, Mr. Todd, a well-known Michigan grower, carried out experiments on a very large scale, and came to the following conclusions :—

1. No loss of essential oil of peppermint through diffusion in the atmosphere is occasioned by thorough drying of the plants and prolonged exposure to atmospheric action prior to distillation.

2. Such exposure does not increase the crystallising tendency of the essential oil.

3. A heavy and insoluble resinoid is produced by oxidation, increasing the specific gravity of the oil and affecting the boiling point and solubility, by raising the former and decreasing the latter.

4. To obtain the best results as to the quality of oil produced and the facility of handling and distillation, the plants should be dried as thoroughly as possible without endangering the loss of leaves and blossom; distillation should then take place as soon as convenient to prevent the formation of resin.

A common form of still used here is a wooden tub or vat made of well seasoned wood, well hooped with iron. Two are kept side by side, so that one can be used whilst the

other is being emptied. The mint is packed into the vat, being trodden down well with the feet, and a steam-tight cover screwed on. Steam is supplied from a boiler to the bottom of the vat, usually at a pressure of from 30 to 40 lb., and the oil and steam are condensed in a worm condenser.

The following details of the method of distillation used in Japan are from a paper published by Mr. E. Marx (*Mitt. der deutschen Gesselschaft für Natur. und Völkerkunde Ostasiens*, vol. vi., p. 335) and translated in the *Chemist and Druggist* (25th April, 1896):—

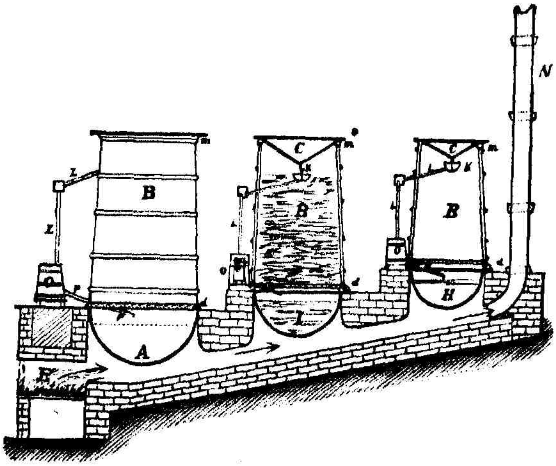


FIG. 17. Peppermint Stills (section).

"From this report we learn that the industry has not benefited by the introduction of European methods, although it is a considerable one. It is Mr. Marx's opinion that the substitution of an improved method for that now followed would benefit both the quantity and quality of the oil produced. The apparatus universally adopted in Japan consists of cast-iron broad-edged boilers, A, I, H; wooden vats, B; and condenser, C. Generally there are three sets of stills, etc., combined in one battery with a common furnace. They

are arranged in steps, so that the lowest is built into the ground.

"The process is begun by filling the boilers, A, I, H, with water; then the vats, B, which have perforated bottoms, are placed on the broad edges and surrounded with straw bands and soft clay. It is in these vats that the peppermint is placed. Next, the inverted condenser, C, is put on and filled with water and the furnace, E, lighted. The heat passes from E below A, I, and H, and disappears through the chimney, N, on which the distilling begins. The boilers, I and H, are properly heated by the fumes as they pass, and sufficiently

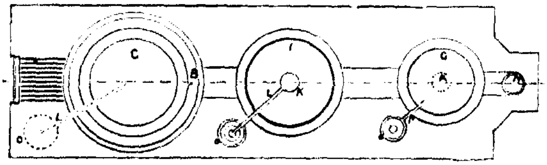


FIG. 18. Peppermint Stills (ground plan).

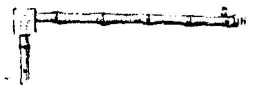


FIG. 19. Bamboo Syphon.

so, as H is smaller than I, and I smaller than A. The steam, penetrating the herb, carries with it the essential oil, and condenses on the outer side of C, being collected in the vessel, K, hanging upon it, from which the condensed water containing the oil passes through a bamboo reed, L, inserted in K to the florentine flasks, O. Each of these consists of a little wooden container in which a glass cylinder (an old bottle without bottom or neck) is inserted. In this, the water separated from the oil runs through the little pipe, P, again into the boilers, A, H, I. As soon as the water in C becomes hot, the workman replaces it with cold water. The emptying is effected by a bamboo syphon. The workman

inserts the short arm in the inverted cooler, closes the lower opening and sucks the syphon until the water flows into it. According to the inborn easy-going nature of the Jap workman, who likes to pause in his work for a smoke, it often happens that the cooling water in C begins to boil and steam runs through instead of the condensed water saturated with oil, so that the atmosphere in the neighbourhood becomes so impregnated with peppermint that any one near loses sight and sense of smell. The workman does not go unpunished, as he burns his mouth by sucking up the boiling water; that, however, does not prevent him from going on smoking, and the same thing happens again. In addition to the direct loss of oil caused by this negligence, it often happens that the water-boiler becomes dry, and then the herb in the still is burnt, in spite of the straw. This sometimes happens in spite of all precautions, as the flames frequently overheat the boilers if the water runs too low, and the products of burning straw get over with the distillate, which explains why Japanese peppermint oil sometimes has a peculiar empyreumatic flavour."

Japanese oil of peppermint contains a very high proportion of menthol, which is frequently removed, and the dementholised oil sold either as such, or, fraudulently, as the natural oil. The usual manner in which the menthol is obtained is by a simple process of freezing, whereby the crystals separate, and are freed from the adherent oil either by pressure or centrifugal treatment. To purify them they should be recrystallised from a suitable solvent, such as alcohol. If it is wished to extract the maximum quantity of menthol, it is advisable to distil off the terpenes, etc., under reduced pressure, and then freeze the residual oil.

Peppermint oil has an extensive use in the preparation of confectionery, liqueurs, etc., and in pharmacy. It is official in the *British Pharmacopœia*, which requires it to have a

specific gravity of ·900 to ·920, and to be soluble in four times its volume of 70 per cent. alcohol. An unsatisfactory qualitative test for menthol is also added; the oil when cool deposits crystals of menthol, it being allowed to add a crystal of this body to induce the crystallisation. This should be replaced by a quantitative determination of the menthol.

Peppermint oil is one of those which improve by keeping, the aroma becoming more delicate, even when kept for ten or twelve years.

Menthol has long been known as the chief constituent of oil of peppermint, and although all the oils of peppermint have not been thoroughly examined, it is probable that the same bodies are in general present in all of them, except in so far as small quantities of some compound or compounds may be present in special oils, modifying the aroma to a considerable extent. For example, the precise difference in the composition of American and English oils is not completely understood. Andres (*Chem. Centr.*, 1890, ii., p. 63) showed that the oil obtained from plants grown in Russia contained the terpene limonene $C_{10}H_{16}$, the hydrocarbon menthene $C_{10}H_{18}$ (which can also be obtained by the dehydration of menthol), menthol $C_{10}H_{19}OH$, and menthone $C_{10}H_{18}O$. Power and Kleber, in 1894, carried out a lengthy investigation of American oil of peppermint, and showed that it contained the following bodies:—

Acetic Aldehyde $CH_3.COH$.	Iso-valeric Aldehyde $C_4H_9.COH$.
Acetic Acid $CH_3.COOH$.	Iso-valeric Acid $C_4H_9.COOH$.
Pinene (*inactive?*) $C_{10}H_{16}$.	Phellandrene $C_{10}H_{16}$.
Limonene (*laevo?*) $C_{10}H_{16}$.	Cineol $C_{10}H_{18}O$.
Menthone $C_{10}H_{18}O$.	Menthol $C_{10}H_{19}.OH$.
Menthyl Acetate $C_{10}H_{19}.C_2H_3O_2$.	Menthyl-iso-valerate $C_{10}H_{19}.C_5H_9O_2$.
Cadinene $C_{15}H_{24}$.	A Lactone $C_{10}H_{16}O_2$.
A Menthyl ester $C_{10}H_{19}.C_8H_{11}O_2$.	

Traces of amyl alcohol and dimethyl sulphide are said to exist in the oil. Charabot in examining French peppermint

oil confirmed the presence of acetic and valeric (iso-valeric ?) acids in the form of esters.

For the chemical examination of peppermint oil, the following characters must be determined. Specific gravity, optical rotation, percentages of free menthol, combined menthol as esters, and of menthone, solubility and (as yielding confirmatory information) behaviour on distillation. Peppermint oil from *Mentha piperita* should have a specific gravity ·900 to ·920, rarely rising to ·925, and an optical rotation usually between – 25° and – 33°, but falling to – 10° or even lower in rare cases.

The Japanese oil from *Mentha arvensis* has a specific gravity of ·895 to ·905, and an optical rotation of – 25° to – 43°. Peppermint oil should be soluble, at most with a trifling opalescence, in four volumes of 70 per cent. alcohol. The method of estimating the menthol (or isomeric menthols —which are possibly present) and the menthone, is by the saponification and acetylation process which was first applied to this oil by Power and Kleber. The total quantity of menthol as esters is first estimated by a preliminary saponification. A quantity of the oil is then saponified and the resulting oil, free from esters, separated and dried. By acetylating this, the menthol is completely converted into menthyl acetate and is estimated by another saponification. This gives the total menthol (in the ester free oil). Another portion of the ester free oil is reduced by means of sodium and alcohol (thus converting the menthone into menthol), and then acetylated and saponified. The amount of menthol now found corresponds to the total menthol originally in the oil together with that formed by reducing the menthone (the difference in the molecular weights of menthol and menthone may here be neglected). The following are the details of the process as given by Power and Kleber :—

About 20 grm. (accurately weighed) of peppermint oil,

together with 30 c.c. of an alcoholic normal solution of sodium hydroxide, are either heated to boiling for an hour in a flask provided with a reflux condenser, or the mixture, contained in a strong, securely-stoppered glass bottle, is heated for an hour in a bath of boiling water, and subsequently the uncombined alkali titrated with normal sulphuric acid with the use of phenol-phthalein as an indicator. From this the combined menthol is calculated as menthyl acetate.

The saponified oil is then repeatedly well washed with water and finally boiled for an hour with an equal volume of acetic anhydride and 2 grm. anhydrous sodium acetate in a flask provided with a suitable condensing tube, ground at one end so as accurately to fit the neck of the flask. The product, after cooling, is washed with water, then with a dilute solution of sodium hydroxide, dried in contact with calcium chloride, and filtered. From 8 to 10 grm. of the resulting oil are then saponified as above, with the use now of 50 c.c. of alcoholic normal solution of sodium hydroxide, and the uncombined alkali determined by titration.

As each cubic centimetre of normal alkali, required for saponification corresponds to 0·156 grm. menthol, and as this yields 0·198 grm. menthyl acetate, it is necessary in order to calculate the found amount of menthol with reference to its percentage in the non-acetylised oil (free from ester) to subtract from the amount of oil used for saponification 0·042 grm. (the difference between 0·156 and 0·198 grm.) for each cubic centimetre of normal alkali consumed. If, for example, *s* grammes of acetylised oil had required for saponification *a* cubic centimetres of normal alkali, the total percentage P of menthol, free and in the state of ester, may be calculated by the following formula:—

$$P = \frac{a \times 15{\cdot}6}{s - (a \times 0{\cdot}042)}.$$

This, indeed, does not indicate with absolute exactness

the percentage of menthol contained in the original oil, for it is assumed in this calculation that all the menthol which is present as ester is combined with acetic acid, whereas as a matter of fact it is partly in combination with iso-valerianic acid, etc. But the error so introduced is so small that it may be left out of account.

As menthone may readily be converted into menthol by reduction, the above-described method may be also employed for the determination of the amount of menthone in the oil, in the following manner. The oil is saponified, and in a portion of the product, previously deprived of alcohol, the percentage of menthol is determined. Another portion is diluted with twice its volume of alcohol, and treated at the boiling temperature of the liquid with metallic sodium. Of the oil which separates by the subsequent addition of water, a weighed quantity is used for another estimation of menthol. The increase corresponds to the amount of menthone present.

The above formula, which gives the total percentage of menthol, is not quite accurate, as it is referred to the ester free (saponified) oil. The correction necessary to be introduced is not of great importance, as the quantity of menthyl esters is not nearly so great as that of free menthol, but to be perfectly correct it must be remembered that to calculate the ester free oil to the original peppermint oil, the latter has lost weight as compared with the former to the extent of ·75 per cent. for 1 each per cent. of KOH required for the preliminary saponification of the esters, assuming that these are all present as menthyl acetate. Thus if an oil gives an ester-content of 10·6 per cent., equivalent to 3 per cent. of KOH, or 8·4 per cent. of menthol, and a total menthol content as calculated from the above formula of 60 per cent., it is necessary to multiply this by the factor $\frac{100}{102 \cdot 3}$ to obtain

the total menthol content in the original oil, *i.e.*, 58·7. Hence the free menthol will be 50·3 per cent., and the combined menthol 8·4 per cent.

With regard to the fractional distillation, it may be noted that the results are very variable, according to the exact conditions of the experiment. But an oil with high menthol content will always give a considerable distillate in the neighbourhood of 215°, which is near the boiling point of menthol (212°).

The accompanying figures for a number of oils are given by Schimmel & Co. (p. 209).

In general, English oils have a specific gravity of about ·906 to ·909, and an optical rotation of − 27° to − 32°, and contain from 60 to 70 per cent. of menthol, or rather more than most American oils. Japanese oils often contain in the natural condition as much as 85 per cent. of menthol. Umney has examined samples of "black" and "white" mint oils comparatively, and gives the following figures for them :—

		Sp. Gravity.	*Rotation.*	*Menthol— as esters.*	*free.*	*Menthone.*
1	Black	·9036	− 23·5°	3·7	59·4	11·3
2	White	·9058	− ·33°	13·6	51·9	9·2

It is necessary to examine a number of samples before generalising on these results.

Charabot has examined a number of French oils (*Bull. Soc. Chim.*, xix., p. 117) which were characterised by their low rotation. His figures are as follows :—

	Sp. Gravity.	*Rotation.*	*Menthol— as esters.*	*free.*	*Menthone.*
1	·921	− 6° 38′	6·6	39·4	9
2	·918	− 6° 40′	5·6	38·7	8·9
3	·918	− 5° 54′	8·0	35·7	8·8
4	·918	− 7° 6′	7·7	37·8	9·6

There is one general conclusion that may be fairly drawn from all these figures; that is, that the effects of climate,

Designation of the Oil.	Specific Gravity at 15° C.	Optical Rotation in a 100 mm. tube.	Menthol in the form of Esters.	Free Menthol.	Total Menthol.	From 50 ccm. of Oil there distil in ccm. between the temperatures noted:								
						? to 200 C.	200-205°	205-210°	210-215°	215-220°	220-225°	225-230°	230-235°	Residue
			%	%	%									
I. F. B., from dry herb	0·9140	– 32° 0′	14·12	45·5	59·6	1·3	1·2	4·3	9·4	12·0	9·8	4·5	1·8	6·1
Ia. F. B., from fresh herb	0·9130	– 30° 0′	11·25	43·2	54·5	0·6	1·2	5·7	8·5	11·6	9·2	4·2	2·2	6·7
Ib. Wayne Co., N.Y., '92	0·9158	– 26° 45′	9·32	40·8	50·1	1·4	1·8	6·3	10·0	12·9	7·3	2·4	1·8	6·3
Ic. " " '93	0·9110	– 32° 30′	9·04	46·1	55·1	1·1	1·4	5·0	10·7	13·9	7·6	2·9	1·6	5·4
Id. " " twice rectified (F. S. & Co.)	0·9110	– 32° 45′	8·61	51·0	59·6	1·5	3·7	8·8	14·7	12·2	4·2	—	—	5·2
Ie. V. B. Co., Mich., '93	0·9067	– 29° 20′	6·39	43·6	50·0	1·9	5·0	9·4	13·2	12·4	2·3	—	—	5·1
If. Wayne Co., Mich., '93	0·9135	– 28° 30′	7·73	50·3	58·0	1·7	1·6	5·5	9·6	12·2	8·9	3·2	3·1	5·8
II. St. J. Co., Mich., '93 (I.)	0·9135	– 9° 45′	3·63	28·9	32·6	1·9	2·6	12·0	14·0	11·6	4·4	—	—	3·3
IIa. " " '93 (II.)	0·9083	– 19° 30′	4·23	29·6	35·8	3·4	7·0	7·6	13·2	10·1	3·3	1·5	—	4·1
IIb. "Rose Mitcham" } Michigan	0·9050	– 23° 35′	4·37	44·2	48·6	4·4	9·6	13·4	17·1	3·2	—	—	—	2·5
IIc. "Crystal White" } Michigan	0·9105	– 23° 55′	5·74	44·2	50·9	1·7	5·8	9·9	15·4	9·4	3·4	—	—	4·1
IId. "Redistilled Oil" } Michigan	0·9165	– 23° 30′	8·59	46·5	55·1	3·3	6·5	8·1	8·8	9·9	5·2	—	—	8·7
III. Mississippi	0·9250	– 13° 40′	11·47	24·2	35·2	0·9	0·3	1·2	6·5	16·2	11·8	4·8	2·4	6·6
IV. Japanese, normal	0·9100	– 34° 45′	3·45	72·7	76·2	0·7	0·4	3·4	22·0	17·2	2·1	1·0	—	3·5
V. " dementholised	0·9030	– 31° 20′	5·71	55·1	60·8	0·5	1·6	10·2	20·7	12·0	3·3	—	—	2·4
VI. Mitcham	0·9070	– 27° 55′	4·92	53·9	58·8	1·4	0·7	12·2	24·7	8·6	—	—	—	3·7
VII. Saxon	0·9100	– 26° 0′	6·38	61·2	67·6	1·7 (? to 205°)		10·9	21·3	11·6	2·1	—	—	2·1

soil and cultivation have a very marked influence on the quality and composition of peppermint oil. For mixtures of the various kinds of these oils, the nose of an experienced dealer is the best test, as a chemical examination, whilst deciding on the purity or otherwise of the oil, will often fail to discriminate between various blends.

Spearmint Oil.—This oil is distilled from the green herb *Mentha viridis*, which yields under ½ per cent. of oil. The spearmint oil of commerce, however, is largely obtained from *Mentha crispa*, but it is practically identical with that from *Mentha viridis*.

So far back as 1864, Gladstone stated that this oil consisted of carvone and a terpene. The results of Trimble and Baeyer confirm this statement, and so far but little further is known of the chemistry of this oil. The *British Pharmacopœia* describes it as being distilled from *Mentha viridis*, and having a specific gravity of ·920 to ·940. Schimmel & Co., however, state that an oil distilled by themselves in America had a specific gravity of ·980, and consider that commercial oils may owe their lower gravity to the fact that the heavier oil is usually left in the still and only the lighter oil collected. This suggestion, however, is most improbable.

A fractional distillation shows a large fraction at 220° to 226°, indicating a high proportion of carvone, usually from 35 to 45 per cent. The optical activity is high, often reaching as much as - 40° or - 50°. The oil should dissolve in an equal volume of 90 per cent. alcohol. This oil is scarcely ever employed in pharmacy, but is used to a limited extent for flavouring and perfumery. The English oil is very expensive, and scarcely ever used, the majority of the oil of commerce being derived from America. A Russian oil of spearmint recently appeared on the market, differing entirely from the ordinary oil. Possibly it is the product of *Mentha aquatica*, or a mixture of this and other species. Its specific

gravity was about ·880 to ·890 and optical rotation from − 20° to − 25°. A sample was examined by Schimmel & Co., and gave the following results. Specific gravity, ·885; optical rotation, − 23° 12′; soluble in two volumes of 70 per cent. alcohol; required 2·6 per cent. of KOH for saponification, and gave an alcohol number calculated as $C_{10}H_{18}O$, by the acetylation process, of 40·6 per cent. The constituents identified were—*laevo*-carvone (5 to 10 per cent.), *laevo*-linalol (50 to 60 per cent.), cineol and *laevo*-limonene (20 per cent.). Other mint oils of little importance are the following:—

Mentha aquatica yields an oil of specific gravity ·880 to ·890 and of variable optical rotation. *Mentha canadensis* yields an oil of specific gravity ·940. Horsemint oil is the product of the American plant *Monarda punctata* (*Mentha sylvestris* is known in England as horsemint, but its oil is unknown). This oil is a slightly dextro-rotary liquid of specific gravity ·930 to ·940. It contains a considerable quantity of terpenes together with cymene, thymol (25 per cent.), an alcohol of the formula $C_{10}H_{18}O$ (linalol?), and traces of formic, acetic and butyric acids.

Pennyroyal Oil.—The leaves and other parts of the plant *Mentha pulegium* yield the ordinary pennyroyal oil. This plant is a native of most parts of Europe, the Caucasus, Chili, Teneriffe, etc. The volatile oil is of a yellow or greenish-yellow colour, and possesses a strong odour of the plant. The specific gravity varies from ·930 to ·960, and the optical rotation from + 16° to + 25°. Several chemists have investigated this oil, but the only well-defined constituent so far identified is the ketone pulegone. The most valued oil is that obtained from Spanish or Algerian plants, but the oil, although used to a certain extent in pharmacy, is now not extensively employed. A Russian pennyroyal oil is known, which is obtained from a different plant, *Pulegium micran-*

thum. This oil has a specific gravity of about ·930, and has an odour recalling peppermint and spearmint. The American pennyroyal oil is distilled from a herb indigenous to North America, *Hedeoma pulegoides*. According to Schimmel, the dried leaves yield about 3 per cent., and the leaves and stalks together about 1·5 per cent. of essential oil. The specific gravity of the sample they examined was ·933, and the optical rotation + 18° 43′. The oil is soluble in two volumes of 70 per cent. alcohol, a characteristic interfered with by the addition of turpentine. The chief ingredient in this oil is pulegone, identical with that from the oil of *Mentha pulegium*.

Mountain Mint Oil is the product of distillation of the herb *Pycnanthemum incanum*, which yields 1 per cent. of an oil of specific gravity about ·910 to ·940, and optical rotation + 3° to + 5°. The oil contains from 7 to 10 per cent. of phenols, chiefly carvacrol, together with some pulegone.

Thyme Oil.—This oil is used to a certain extent for veterinary purposes and cheap soap perfumery, often under the name of *Origanum oil* (which is in reality the product of a species of *Origanum*). The most valued oil is the Spanish distillate, which is the product of *Thymus vulgaris*; a good deal of oil is produced in the south of France, but this is frequently mixed with the oil of *Thymus serpyllum*, and also very frequently adulterated with turpentine. Two commercial varieties are recognised, the "red" and "white" oils. The former is the crude distillate, and probably owes its red colour to the action of the phenols present on the iron of the crude stills and condensers frequently used. The red oil when properly rectified forms the colourless or "white" oil of commerce. The yield of oil is very variable—sometimes being as low as ·5 per cent., often rising to 1 per cent. in the fresh and 2·5 per cent. in the dried herb. The oil contains from 20 to 30 per cent. of phenols, chiefly thymol and car-

vacrol, upon which the value of the oil chiefly depends. As these are sometimes fraudulently removed, it is important that the percentage of phenols should be the basis of valuing the oil. In addition to the phenols, there also occur pinene, cymene, borneol, linalol and bornyl acetate. The genuine oil usually possesses a specific gravity ·905 to ·935 and is slightly laevo-rotary. Admixture with the oil of *Thymus serpyllum* does not alter the specific gravity, but increases the rotation, as this oil rotates up to $-12°$. Oils adulterated with French turpentine have a high laevo-rotation. A very large amount of the French "white" oil contains a considerable quantity of turpentine. The percentage of phenols is indicated by the decrease in volume on shaking with aqueous solution of potash, and also by the amount of oil distilling above 220°, which should not fall below 25 per cent. Kremers recommends the following method of estimating the thymol:—

5 c.c. of the oil to be examined is weighed and brought into a glass-stoppered burette graduated to $\frac{1}{10}$ c.c., and is diluted with about an equal volume of petroleum ether; a 5 per cent. potassium hydroxide solution is added, and the mixture shaken for a short time, then the liquid is left standing until separation is complete. Then the alkaline solution is allowed to run into a 100 c.c. graduated flask. This operation is repeated until no further decrease in the volume of the oil takes place.

The alkaline solution of thymol is made up to 100 or 200 c.c. as the case may require, using a 5 per cent. soda solution. To 10 c.c. of this solution in a graduated 500 c.c. flask is added a $\frac{1}{10}$ normal iodine solution in slight excess, whereupon the thymol is precipitated as a dark reddish-brown iodine compound. In order to ascertain whether a sufficient quantity of iodine has been added, a few drops are transferred into a test tube and a few drops of dilute hydrochloric acid are

added. When enough iodine is present, the brown colour of the solution indicates the presence of iodine, otherwise the liquid appears milky by the separation of thymol. If an excess of iodine is present, the solution is slightly acidified with dilute hydrochloric acid and diluted to 500 c.c. From this, 100 c.c. are filtered off, and the excess of iodine determined by titration with $\frac{1}{10}$ normal solution of sodium thiosulphate. For calculation, the number of c.c. required, multiplied by 5, and deducted from the number of c.c. of $\frac{1}{10}$ normal iodine solution added, gives the number of c.c. of iodine required by the thymol.

Every c.c. of $\frac{1}{10}$ normal iodine solution equals 0·003741 grm. of thymol. Knowing the quantity of thymol in the alkaline solution, the percentage in the original oil is readily found.

The reaction taking place is represented by the equation:—

$$C_{10}H_{14}O + 4I + 2NaOH = C_{10}H_{12}I_2O + 2NaI + 2H_2O.$$

In the estimation of carvacrol a slight modification of this method must be made, because carvacrol is thrown down as a finely divided white precipitate, giving the solution a milky appearance. In order to form a precipitate the liquid is vigorously shaken after the addition of the iodine solution, and is subsequently filtered. Then the liquid is acidulated with hydrochloric acid, and subsequently the same procedure is followed as was described for thymol. The calculation is also the same.

Labbé has examined an authentic sample of thyme oil (*Bull. Soc. Chim.*, iii., 19, 1009) and found it to contain 30 per cent. of thymol, 17 per cent. of a terpene which he could not identify, 15 per cent. of menthene, 21 per cent. of cymene, 5 per cent. of linalol, 8 per cent. of borneol, and traces of carvacrol.

Thymus capitatus also yields an oil of specific gravity

about ·900, and closely resembling the above-described oils. It contains pinene, cymene, dipentene, thymol, carvacrol and bornyl acetate. A similar oil is obtained from *Thymus camphoratus*. A somewhat different oil is obtained from a variety of *Thymus serpyllum* (*citratus* or *citriodorus*). This oil has an odour recalling thyme, lemon and geranium.

The value of this oil depends so much upon the phenols it contains that it is important that these should be estimated, as the abstraction of thymol, a valuable commercial product, is by no means uncommon.

Marjoram and Origanum Oils.—Common marjoram oil is the product of distillation of the herb *Origanum vulgare*, sweet marjoram oil being derived from *Origanum majorana*. The Cretic origanum oil is the product of *Origanum hirtum* and *Origanum Smyrnæum*. The marjoram oils have a specific gravity of ·890 to ·910, and are dextro-rotary to the extent of + 20°. Although they resemble oil of thyme, their chemistry has not been completely investigated. The Cretian origanum oil (Spanish hop oil) differs in a marked manner from the marjoram oils. That from *Origanum hirtum* has a specific gravity of ·940 to ·980, and is optically inactive or only slightly laevo-rotary. That from *Origanum Smyrnæum* has a specific gravity ·915 to ·945, and is laevo-rotary from - 3° to - 15°. The former contains from 60 to 85 per cent. of phenols, chiefly carvacrol, together with some cymene. The latter has been examined by Schimmel & Co. and found to contain from 30 to 60 per cent. of phenols, chiefly carvacrol, together with cymene, and one or more hydrocarbons, probably of the naphthene series, and a large quantity of linalol. A phenol is also present in minute quantity which has not been identified. The ordinary oil of marjoram is only worth about half as much as "*Ol. Origani Cretic*," which is used for microscopic purposes. Both are often adulterated with turpentine.

Biltz (*Berichte*, 1899, 995) has recently examined a sample of pure oil of *Origanum majorana*, which had a specific gravity ·898, and a rotation of +15° 45′. The terpenes (about 40 per cent.) were found to consist chiefly of terpinene. Terpineol and terpenyl esters were also found, the latter chiefly existing as terpinyl acetate (6 per cent).

Patchouli Oil is distilled from the dried leaves of *Pogostemon patchouli*, which yields from 2 to 4 per cent. of oil. This plant is possibly a native of China, but is cultivated to a large extent in the Straits Settlements, Penang, Silhet, Java, Bourbon and Mauritius. There appear to be several varieties, and although one is usually employed for the preparation of the oil, others are not excluded. According to Mr. Fisher (the well-known Singapore distiller), the variety selected for cultivation is known locally as "*Dhelum Wangi*". The green tops of the plant are dried in the shade in large sheds and spread out on bamboo racks, being turned over frequently. It is important that they should not be sun-dried, however. About 25 per cent. of the leaves of the wild plant known as "*Dhelum outan*" are added, as it is said to increase the fragrance of the resulting oil. The distillation is carried out in false-bottom cylinders, using steam at a pressure of about 10 to 15 lb. In Penang two varieties of oil are known, the green and the brown. It has been suggested that the former is obtained from young, and the latter from old leaves, but it is more probable that the differences are due to the influence of soil and climate. Interesting details as to the cultivation of the plant will be found in Sawyer's *Odorographia* (vol. i., p. 293). Although pure oil distilled in the East is easily obtainable, the fraud practised in certain quarters led to direct importation of the leaves, which are now distilled in Europe. The pure oil has a specific gravity of ·975 to ·995, and an optical rotation of − 50° to − 65°. Its favourite adulterants appear to be cedar-wood oil, cubeb oil,

and occasionally turpentine and petroleum. The pure oil should dissolve in an equal volume of 90 per cent. alcohol, the two last-named adulterants interfering greatly with this property.

The earliest chemical examination of this oil was made by Dr. Gladstone in 1864, who stated that it contained a hydrocarbon analogous to that from oil of cubebs, together with a small quantity of an intensely blue colouring matter which he termed cærulein. Gal and Montgolfier have more recently shown that the oil contains a solid body, which they termed patchouli camphor, and which Wallach has shown to be a sesquiterpene alcohol $C_{15}H_{26}O$. This body is probably the oxidation product of other substances in the oil, and appears to have little or no odoriferous value. It is deposited when the oil stands for long in a cold place. When re-crystallised it melts at 56°. Dehydration gives rise to a hydrocarbon $C_{15}H_{24}$ patchoulene. The sesquiterpene occurring naturally in the oil has been shown to be cadinene, but as this body occurs in juniper oil and in the oil of cade, it is clear that the odorous substance of patchouli oil is still undiscovered.

The fresh leaves of patchouli have been distilled and the oil examined. This was found to have a specific gravity ·943 and optical rotation − 11° 30′. Patchouli oil was once regarded as one of the high class perfume bases, but its use became a little unpopular, and its price declined, fine distillates being now obtainable for about 16s. or 18s. per lb., so that it is now more frequently employed in lower-grade perfumery.

Melissa Oil.—This oil, also known as *balm oil*, is distilled from the green herb *Melissa officinalis*. Several species are indigenous to western Asia and southern Europe. The leaves possess an odour recalling lemon and citronella (the French *citronelle* is this plant), but the yield of oil is so small, that the melissa oil of commerce is usually obtained

by distilling lemon or citronella oil, or a mixture of both, over the herbs. The genuine oil has been examined by Schimmel & Co., who state that it has a specific gravity from ·890 to ·925, and a rotation of + 0° 30′ to + 6° 30′. It contains citral and probably citronellal. Flatau and Labbé state (*Bull. Soc. Chim.*, 1898, iii., 636) that a specimen they examined contained 20 per cent. of geraniol, 12 per cent. of linalol, and 6 per cent. of citronellol. Its use is entirely confined to perfumery purposes.

Sage Oil is distilled from the leaves of *Salvia officinalis*, which yield from 1 to 3 per cent. of oil. This is of a pale yellow to greenish-yellow colour and of penetrating odour. Its specific gravity varies from ·915 to ·930, and its rotation from + 10° to + 25°. The known constituents of the oil are the terpene pinene, a sesquiterpene, cineol, borneol and thujone. Muir, working from 1877 to 1880 on this oil, stated that it contained a terpene identical with that from turpentine (pinene), a sesquiterpene which he termed sage-cedrene, a solid "camphor" $C_{10}H_{16}O$, and salviol, which Semmler has shown is identical with thujone. The oil is only employed to a very limited extent. *Salvia sclarea* also yields an oil with a highly aromatic odour, recalling that of ambergris. It is known commercially as *clary* oil. The oil has a specific gravity about ·930 and an optical rotation of about − 25°. It probably contains linalyl acetate.

Savory Oil.—The oil distilled from the green herb winter savory, *Satureja montana*, has been examined by Haller, who states that it is an orange-yellow oil of aromatic taste, somewhat resembling true origanum oil, of specific gravity ·937. He found in it from 30 to 40 per cent. of carvacrol, and traces of another phenol. Two hydrocarbons at least are present, probably cymene and a terpene. A sample examined by Schimmel & Co. had a specific gravity ·939 and optical rotation − 2° 35′. It was soluble in 4·5 volumes of 70 per cent.

alcohol, and contained 65 per cent. of phenols. The oil of the summer savory, *Satureja hortensis*, does not differ greatly from that of the winter savory. According to Schimmel, this has a specific gravity ·913 to ·924, and contains carvacrol and cymene. Jahns has examined the oil, but as the sample he used had a specific gravity ·898 it is probable that it was adulterated with turpentine. He found 30 per cent. of carvacrol in the oil, with traces of a second phenol, cymene, and one or more terpenes. *Satureja thymbra* also yields an oil of specific gravity ·906 which contains pinene, cyenene, dipentene and bornyl acetate.

Sweet Basil Oil.—This oil is distilled from the fresh herb *Ocymum basilicum*, which, according to Schimmel, yields about $\frac{1}{30}$ per cent. of essential oil. Other authorities, however, give as high a yield as $1\frac{1}{4}$ per cent. The former appears to refer to German herbs, whilst the latter refers to the fine Réunion or Java distillate. This oil has a most excellent fragrance, and is used in the preparation of mignonette extract. The oil has a specific gravity ·909 to ·990, and an optical rotation varying from + 15° to − 20°. The old text books gave "Basil camphor" as its known constituent, which separates in crystals when the oil is kept. Dupont and Guerlain were the first to attempt a thorough examination of this oil. They first examined a French distillate, and found in it methyl-chavicol (*estragol*) and *laevo*-linalol. Schimmel & Co. examined a Réunion oil, and found methyl-chavicol to be the chief constituent of this also. As secondary constituents they found pinene, camphor and cineol. An oil grown at Miltitz, however, contained only 25 per cent. of methyl-chavicol, and differed much in odour from the Réunion oil. This oil contained some cineol, together with an alcohol (probably linalol), but no camphor. Dumas and Péligot some time ago stated that they had discovered a crystalline terpene hydrate in this oil, but neither

Dupont and Guerlain nor Messrs. Schimmel & Co. have been able to find this. Traces of a crystalline substance melting at 64° were found in Réunion oil, but in too small quantity to be examined. French and German oils are laevo-rotary, whilst the Réunion distillate is dextro-rotary and has a somewhat more camphoraceous odour than European oils. Further, it contains no linalol. It is a matter of some doubt whether the Réunion plants are *Ocymum basilicum* or some other species.

The following are among the less important oils distilled from plants of the natural order *Labiatæ*. *Hyssop Oil*, from the herb *Hyssopus officinalis*, used to a small extent in perfumery and for the preparation of cordials. Its specific gravity is ·925 to ·940, and optical rotation – 19° to – 23°. The southern regions of the Harz mountains are said to yield the finest material for distillation, but the French and Spanish oils are much esteemed. *Catmint Oil*, from the herb *Nepeta cataria*, specific gravity about 1·040. *Bugle Weed Oil*, from the dried herb *Lycopus virginicus*, specific gravity ·924. *Ground Ivy Oil*, from the herb *Glechoma hederacea*, specific gravity ·925. *Dittany Oil* (American), from the herb *Cunila mariana*; this oil has a specific gravity ·915 and probably contains thymol. The total phenol content is about 40 per cent.

N. O. VERBENACEÆ.

Verbena Oil.—Most of the commercial verbena oils and verbena extracts are in reality composed of lemon-grass oil, which has almost entirely superseded the older and true vervain oil. The genuine oil closely resembles lemon-grass oil in general characteristics, but is of more delicate odour. It contains a large quantity of citral, and has a specific gravity about ·890 to ·900. The plants yielding this oil appear to be *Verbena officinalis* and *Verbena triphylla*. But

in Spain a plant known as *Aloysia citriodora* or *Lippia citriodora* yields "verbena oil". This, however, is possibly not one of the *Verbenaceæ* at all. The exact character of true verbena oil is somewhat obscure on account of the almost universal use of lemon-grass oil under this name. *Lantana camara*, one of the plants of this natural order, also yields an essential oil. This has a specific gravity ·950 to ·955, and is optically inactive or at most slightly laevo-rotary.

N. O. Convolvulaceæ.

Rosewood Oil.—Rosewood oil or rhodium oil as met with in commerce is almost, if not quite, invariably an artificial mixture of several essential oils in which true oil of roses and oil of geranium or Indian geranium are responsible for the rose or rose-geranium odour. The true oil of rhodium is distilled from the wood either of the stem or the root of *Convolvulus scoparius* and *Convolvulus floridus*, two species indigenous to the Canary Islands. It is a thick, viscid, pale yellow oil, darkening on keeping. It has an agreeable rose-like odour and sharp aromatic taste. Its specific gravity varies from about ·900 to ·910. It is laevo-rotary. According to Gladstone, it contains 80 per cent. of a terpene; but the authenticity of the sample examined by this chemist is not guaranteed. It is more probable that a large quantity of sesquiterpene is present. According to Schimmel & Co., the oil solidifies at low temperatures to a mass of acicular crystals melting at 11° to 12°. The oil is chiefly used in soap perfumery. The *Bois de rose femelle* is the wood of the so-called Brazilian lign-aloe, and yields the corresponding linaloe oil. It is one of the Burseraceae, and has no connection with the above described rosewood.

N. O. JASMINEÆ.

Jasmin Oil.—The perfume of the jasmin is one of those which is usually obtained by the process of enfleurage, such as are those of the tuberose, jonquil, hyacinth, etc. By direct distillation so minute a yield of essential oil is obtained from these plants, that the perfumes are only known in the form of pomades or extracts. The pomade of jasmin flowers, however, yields to suitable solvents, acetone for example, sufficient of the essential oil for thorough examination. The species of this plant are very numerous, but that chiefly used for the preparation of the pomade in the south of France is *Jasminum grandiflorum*, the shoots of which are usually grafted on the stems of the *Jasminum officinale*, which are themselves reared from cuttings. Quite recently some great differences of opinion have been expressed as to the composition of this oil. Verley (*Comptes Rendus*, 30th Jan., 1899) extracted the pomade with acetone and obtained, after evaporation of this solvent *in vacuo*, 40 grammes of oil, which on distillation *in vacuo* left 40 per cent. of resin and yielded 60 per cent. of essential oil. Verley concluded that the oil was approximately composed of 10 per cent. of linalol and 90 per cent. of phenyl-glycol-methylene-acetal ($C_9H_{10}O_2$). These researches led to the granting of a French patent for the production of this body synthetically, as an artificial jasmin oil. The specification states that 50 grammes of phenol-glycol, 30 grammes of sulphuric acid, diluted with 125 grammes of water, and 100 grammes of formic aldehyde are to be heated on a water bath. The resulting body when purified boils at 218°, and is said to have a strong jasmin odour. On the other hand, Hesse and Müller, who have examined a very large number of samples of this oil, state that they have most carefully examined the oil and assert that there is not a trace of this body present, but that the main constituent is benzyl acetate. The following are the figures

they give for ten samples of oil prepared by themselves from the pomade:—

No.	Yield per cent.	Specific Gravity.	Rotation.	Esters—calculated as	
				Linalyl acetate.	Benzyl acetate.
				Per cent.	Per cent.
1	·427	1·015	+ 2° 30′	95·4	73·0
2	·457	1·018	+ 2° 30′	91·5	70·0
3	·429	1·011	+ 2° 30′	95·0	72·9
4	·473	1·009	+ 3° 30′	92·0	70·4
5	·409	1·006	+ 3° 15′	90·3	69·1
6	·395	1·007	+ 3° 10′	90·9	70·7
7	·595	1·014	+ 3° 20′	92·8	71·0
8	·490	1·012	+ 3° 10′	94·1	72·0
9	·526	1·009	+ 3° 30′	95·4	73·0
10	·480	1·015	+ 3° 20′	93·3	71·4

They have made a very careful and exhaustive examination of the oil, and have studied quantitative methods for estimating its components, which finally leads them to the conclusion that the average composition of the oil is as follows:—

	Per cent.
Benzyl acetate	65
Linalyl acetate	7·5
Benzyl alcohol	6
Linalol	16
Other odorous bodies	5·5

(The work of these chemists, which is certainly the most valuable contribution to the chemistry of this oil, may be found in full in the *Berichte*, 1899, pp. 565 and 765).

There is another compound which can easily be prepared artificially which has a distinct jasmin odour. The styrolene compounds are, as a group, remarkable in that they often possess floral odours. Thus, the *alpha*-substitution products of styrolene $C_6H_5 . CH : CH_2$, such as bromstyrolene $C_6H_5 . CH : CHBr$, have usually a distinct hyacinth-like odour. Styrolene alcohol $C_6H_5 . CH(OH)CH_2OH$ is

identical with phenyl-glycol, the basis of the above-mentioned French patent; whilst *secondary* styrolyl acetate C_6H_5. $CH(O.CO.CH_3)CH_3$ has itself a marked odour of jasmin. This body can be prepared by the action of bromine on boiling ethyl-benzene. The resulting bromide is heated with silver acetate and glacial acetic acid, yielding styrolyl acetate.

Artificial oil of jasmin compounded on the lines of the above-mentioned facts is now a regular article of commerce and is worth from 12s. to 15s. per ounce. It closely resembles the natural perfume, except that it is less delicate; and is well adapted for high-class toilet perfumery.

N. O. ERICACEÆ.

Oil of Wintergreen.—This oil is one of those which is so closely imitated by other oils (*vide Oil of Verbena*) that the commercial article is very seldom the true oil at all. Genuine wintergreen oil is the product of distillation of the leaves of *Gaultheria procumbens;* "commercial" wintergreen oil is almost invariably the product of distillation of the bark of *Betula lenta*, one of the *Cupuliferæ* (*q.v.*); or an artificial synthetic oil, methyl salicylate. *Gaultheria procumbens* is a plant of North America, known as the tea berry or partridge berry. The leaves are gathered and distilled in primitive apparatus, either ordinary whisky stills, or stills composed of wooden tubs with copper bottoms. The resulting oil, which is yielded to the extent of ·5 to 1 per cent., has a specific gravity 1·177 to 1·187, and is faintly laevo-rotary (under − 1°). The bark of *Betula lenta*, the sweet birch, yields about the same quantity of an oil of so exactly similar nature that it is now sold as oil of wintergreen to the almost entire exclusion of the true *Gaultheria* oil. In this plant the oil is the product of decomposition of the glucoside gaultherine. The only physical difference is that it is quite inactive

optically, both oils being almost pure methyl salicylate $C_6H_4 . OH . CO_2CH_3$. Cahours (*Liebig's Annalen*, lii., p. 331) was the earliest reliable investigator of wintergreen oil, but his work has been shown to be only partially correct. According to him the oil consisted of about 90 per cent. of methyl salicylate and 10 per cent. of a terpene, which he named gaultheriline. Probably he examined an adulterated oil. Trimble and Schroeter (*Amer. Chem. Jour.*, 1889, p. 398) stated that both oil of wintergreen and oil of birch contained traces of benzoic acid and ethyl alcohol, together with under 0·5 per cent. of a hydrocarbon (different in the two oils). Power and Kleber, however, have examined a very large number of samples, and give as the result of their work the following summary :—

"*Oil of Gaultheria.*—Contains about 99 per cent. of methyl salicylate, together with a small amount of a paraffin, probably triacontane $C_{30}H_{62}$, an aldehyde or ketone, an apparently secondary alcohol $C_8H_{16}O$, and an ester $C_{14}H_{24}O_2$. To the latter body is possibly due the optical activity of the oil, whereas in the oil of birch it may be assumed that this body has suffered inversion through the process of fermentation by which the latter oil is formed.

"A pure fresh oil of gaultheria should show an optical rotation of not less than $- 0° 25'$ in a tube of 100 mm.

"*Oil of Sweet Birch.*—This oil consists to the extent of about 99·8 per cent. of methyl salicylate, and, in its unrectified state, contains also a very small amount of the above-mentioned paraffin $C_{30}H_{62}$, and the ester $C_{14}H_{24}O_2$, but does not contain the alcohol $C_8H_{16}O$ which is found in gaultheria oil.

"The oil of sweet birch is always optically inactive.

"Both of these oils have a specific gravity ranging usually from 1·180 to 1·187 at 15° C. Both of them, as well as the synthetic methyl salicylate, form a perfectly clear solution

with five (5) times their volume of 70 per cent. alcohol at about 20° C., which, in connection with other distinctive characters, is an excellent practical test for their purity.

"Neither the oil of gaultheria nor the oil of sweet birch contains any trace of benzoic acid or its esters, nor do either of them contain any terpene or sesquiterpene."

The above facts easily explain the appearance on the market of artificial methyl salicylate, which is easily prepared by a condensation of methyl alcohol and salicylic acid. It has been objected that the odour of the artificial oil is not so fragrant as that of the natural oil, but so long as the salicylic acid used in its manufacture is pure, no exception can be taken to it. As the synthetic oil is worth less than half the value of the natural product of *Betula lenta*, and mixtures of the two are impossible to detect, it is easy to understand how the producing districts in America started importing the *artificial* oil, which returns to commerce as *natural* oil. The purchase of this oil, so far as its origin is concerned, must therefore be largely a matter of trust in the seller. With the exception of the fact that the true oil of *Gaultheria* is faintly laevo-rotary whilst the oil of *Betula* and the synthetic oil are optically inactive, the limits as regards physical and chemical characters are identical for the three oils. The specific gravity should never vary outside the limits 1·177 to 1·187. The oil should give a clear solution with five times its volume of 70 per cent. alcohol. On saponification with alcoholic solution of potash, the oil should give a result equivalent to at least 98 per cent. of methyl salicylate. The salicylic acid resulting from the addition of acid to the saponification product, after a single recrystallisation from alcohol, should melt at 155° to 157°. This will guard against the use of impure salicylic acid in the preparation of the artificial oil.

This oil is often adulterated with petroleum or light

camphor oils, both quite easy of detection; also with sassafras oil, which, in spite of its high specific gravity, is easily detected by its lowering the saponification number, and its characteristic odour remaining after the wintergreen odour has been destroyed by saponification. The oil is used to a certain extent in pharmacy, either as a drug or to cover the nauseous taste of other drugs, but more extensively as a flavouring in the manufacture of such confections as the American chewing gum. Methyl salicylate has been detected in the following plants:—

	Discoverer.	*Year of Discovery.*
BETULACEÆ.		
Betula lenta L.	Wm. Procter, jr.	1844
Betula lutea Mich. probably, but not yet determined.		
LAURACEÆ.		
Lindera Benzoïn Meissner	Schimmel & Co.	1885
ROSACEÆ.		
Spiræa ulmaria L.	Schneegans & Gerock	1892
ERYTHROXYLACEÆ.		
Erythroxylon coca Lam.	v. Romburgh	1894
Erythroxylon bolivianum (?)	v. Romburgh	1894
POLYGALACEÆ.		
Polygala senega L.	Langbeck	1881
Polygala senega var. latif. Torr. and Gray	L. Reuter	1889
Polygala baldwinii Nuttall	J. Maisch	1890
Polygala variab. H. B. K. *albifl.* D. C.	v. Romburgh	1894
Polygala javana D. C.	v. Romburgh	1894
Polygala oleïfera Heckel	v. Romburgh	1894
Polygala serpyllacea Weihe (*depressa* Warden).	Bourquelot	1894
Polygala calcarea F. Schultz	Bourquelot	1894
Polygala vulgaris L.	Bourquelot	1894
PYROLACEÆ.		
Hypopitys multiflora Scop. (*Monotropa Hypop.* L.).	Bourquelot	1894
TERNSTRŒMIACEÆ.		
Thea chinensis	Schimmel & Co.	1897

Ericaceæ.	Discoverer.	Year of Discovery.
Andromeda Leschenaultii	Broughton	——
Gaultheria procumbens L.	Cahours	1843
Gaultheria fragrantissima Wall.	Broughton	1867
(*Gaultheria punctata* Blume / *Gaultheria Leschenaultii*, D.C.) / *Gaultheria leucocarpa* Blume	Koehler	1879

The author has also detected traces of it in some plants of the natural order *Violaceæ*.

Marsh Tea Oil.—*Ledum palustre*, a plant of this natural order yields from ½ to 1 per cent. of an essential oil. The plant is one flourishing in marshy places in the northern parts of North America, Asia and Europe. The leaves and flowering twigs are used for distillation, and the oil obtained is of a reddish-yellow colour and sharp taste and odour. The oil appears to consist almost entirely of a sesquiterpene alcohol $C_{15}H_{26}O$, which has been termed ledum camphor, and a sesquiterpene possibly identical with that obtained by treating the camphor with dehydrating agents, and which has been named ledene. Ledum camphor forms long white needles, melting at 104° and boiling at 282°, and is feebly dextro-rotary. The oil possesses strongly narcotic properties, and is said to be occasionally illicitly added to beer to render it more intoxicating. This, however, is very doubtful. The oil from the leaves has a specific gravity of ·925 to ·935, and that from the flowering twigs about ·960.

N. O. Valerianeæ.

Valerian Oil.—The ordinary oil of valerian is obtained by the distillation of the root of *Valeriana officinalis*. The Dutch and Thuringian herb was mostly used on the continent for distillation until the recent introduction of the Japanese root (from the variety *angustifolia*), which yields from 6 to 7 per cent. of oil as against 1 per cent. for the

European root. The oils from the two varieties are quite similar, and may be used indiscriminately. That from the European plants has a specific gravity of ·930 to ·960, and an optical rotation of − 8° to − 15°, whilst that from the Japanese variety (known also as Kessö oil) has a specific gravity ·985 to ·995, and is laevo-rotary to about the same extent as the European oil.

Pierlot investigated this oil some years ago, but his results cannot be accepted in the light of our present knowledge of essential oils. Oliviero has carefully examined the European oil, and finds in it the terpenes pinene, camphene and limonene; borneol and its formic, acetic and iso-valerianic esters, terpineol, and probably a sesquiterpene, a sesquiterpene alcohol $C_{15}H_{26}O$, and a crystalline bivalent alcohol of the formula $C_{10}H_{20}O_2$, melting at 132°. Bertram and Guildemeister have examined the Kesso oil and found in it the terpenes pinene, camphene and dipentene, terpineol, borneol, bornyl acetate and bornyl iso-valerianate, a sesquiterpene, a blue oil not identified, and kessyl acetate $C_{14}H_{23}O \cdot CO_2CH_3$. This body is the acetic ester of kessyl alcohol $C_{14}H_{24}O_2$, a liquid boiling at 300°, whose chemical relationships are not yet established.

Valerian oil is employed to a considerable extent on the continent as a popular remedy for cholera, in the form of cholera drops, and also to a certain extent in soap perfumery.

Valeriana Celtica, a native of the Swiss Alps and the Tyrol, yields an essential oil with an odour recalling patchouli and chamomiles. Its specific gravity is ·960 to ·970. The yield is about 1 per cent. Messrs. Schimmel & Co. distilled a parcel of Mexican root which was probably *Valeriana Mexicana*, known locally as *cuittapatti*. The oil had a disagreeable odour of valerianic acid; its specific gravity was ·949, and it was optically inactive. It appears to consist almost entirely of hydrated valerianic acid.

Oil of Spikenard.—This oil, which is the true spikenard or Indian spikenard, has been described as being obtained from various plants, but there now appears to be no doubt that it is obtained from *Nardostachys Jatamansi*, a plant flourishing in the Alpine Himalayas and district. Kemp distilled 56 lb. of the root and obtained 3 oz. of oil, whilst another parcel of 100 lb. yielded 15 oz. It is a pale yellow oil of specific gravity ·975, and optical rotation about − 20°. Although its odour may be considered disagreeable by many, it is highly esteemed in the East as a perfume. Its use is practically replaced in western countries by that of oil of valerian.

N. O. Compositæ.

This extensive natural order yields a large number of essential oils, but the majority are of small commercial importance.

Chamomile Oil.—There are two varieties of this oil, the Roman chamomile oil, distilled from the flowers of *Anthemis nobilis*, a plant indigenous to the southern and western parts of Europe, and cultivated in Germany, Great Britain, France and Belgium; and the German chamomile oil distilled from the flowers of *Matricaria chamomilla*.

Roman chamomile oil, which is the oil official in the *British Pharmacopœia*, is obtained to the extent of 1 per cent. from the recently dried flowers. When first distilled it is of a blue colour, but usually turns to a greenish or greenish-yellow colour on keeping. It has a characteristic flavour and odour, but not of the nature to justify its use in perfumery. Its specific gravity varies from ·905 to ·915. It is chiefly composed of esters of angelic and tiglic acids, two isomeric acids of the formula $C_5H_8O_2$. The following esters have been identified: isobutyl isobutyrate, isobutyl angelate, amyl angelate, amyl tiglate, hexyl angelate, hexyl

tiglate, and possibly esters of an alcohol anthemol, $C_{10}H_{15}OH$. Traces of the free alcohols and acids, probably due to decomposition of the esters during distillation, also exist. Naudin (*Bull. Soc. Chim.*, xli., p. 483) obtained from the flowers, by extraction with light petroleum, two crystalline substances not included in the above list. One of these he terms anthemene, and considers it to be a hydrocarbon $C_{18}H_{36}$ of the ethylene series. It forms microscopic needles melting at 63°.

German chamomile oil from *Matricaria chamomilla* has a specific gravity ·930 to ·940. Its colour is intensely blue, often turning greenish-blue on keeping. It is a thick fluid becoming semi-solid on cooling, commencing to thicken at about 14° and congealing at 1°. It is freely soluble in 90 per cent. alcohol. According to older researches, which are not reliable, the oil consists of chamomillol $C_{10}H_{16}O$, a terpene, and trichamomillol $C_{30}H_{48}O_3$ (the blue portion of the oil). As a matter of fact the only constituents whose identity have been definitely proved are esters of caproic acid, with traces of their decomposition products, together with a solid hydrocarbon or mixture of hydrocarbons, which is probably responsible for the solidification of the oil at low temperatures. This body (or mixture) melts at 53° to 54°, and when perfectly pure is quite white. Messrs. Schimmel & Co. consider it to be a hydrocarbon or hydrocarbons of the paraffin series. Possibly it contains the bodies previously isolated from Roman chamomile oil by Naudin (*vide supra*). The exact nature of the blue constituent of the oil is not known. Probably it is identical with that existing in wormwood oil.

Chamomile oil is often adulterated with cedar and turpentine oils, sometimes with copaiba oil, and, according to some authorities, with milfoil oil. Some of the commercial oil is merely turpentine or lemon oil or a mixture of these oils, distilled over chamomiles. This reprehensible custom

of selling low-priced rubbish under unjustifiable names is countenanced by even reputable firms, who offer in their price lists "chamomile oil" and "chamomile oil with lemon," the latter at about one-fifth of the price of the former.

Feverfew Oil.—The common feverfew, *Pyrethrum parthenium* (*Matricaria parthenium*), yields a small amount of essential oil of strong, characteristic odour. The green flowering herb yields about ·07 to ·4 per cent. of an oil of specific gravity ·900 to ·960. The dried herb yields rather less oil than the fresh plant. Chantard investigated this oil and stated that it contained a terpene and an oxygenated body resembling camphor. In all probability this oxygenated body is a mixture of camphor and borneol. Schimmel & Co. obtained ·068 per cent. of oil from the herbs, which had a specific gravity ·960. Even at the ordinary temperature it contained a considerable number of hexagonal crystals, which appear to be borneol. Bornyl esters are also present, but no camphor could be detected.

Wormwood Oil.—This oil is distilled from the green herb *Artemisia absinthium*, a plant indigenous to the hilly and mountainous regions of northern Africa, Europe and the north of Asia, and cultivated to a considerable extent in North America. The yield varies from ·2 to ·9 per cent. The oil is of a greenish or greenish-blue colour, and of characteristic odour and taste. It is frequently known as oil of absinthe. The pure oil has a specific gravity ·925 to ·955. It contains a considerable proportion of the ketone thujone. Schimmel & Co. have investigated it, and find a very small quantity of phellandrene and the merest traces of pinene present. In addition to these bodies, the oil contains free thujyl alcohol and its acetic, isovaleric, and palmitic esters. A pure sample examined by means of the acetylation and saponification methods gave results equivalent to 14 per cent. of thujyl alcohol and 15 per cent. of thujyl acetate. The oil

is frequently adulterated, the favourite adulterant being turpentine. This is best detected (Schimmel) by distilling 10 per cent. from the oil. This fraction should dissolve to a clear solution in twice its volume of 80 per cent. alcohol. The presence of even a very small amount of turpentine upsets this test. Wormwood oil has a tonic and stimulating effect on the digestive organs, and is sometimes also used externally. It is a constituent of the well-known liqueur, absinthe.

Wormseed Oil.—Ordinary wormseed oil (*Oleum cinæ*) is the product of distillation of the unexpanded flower buds of *Artemisia maritima*, although other species probably contribute to the commercial oil. ("American wormseed" oil is the product of one of the *Chenopodiaceæ, q.v.*). The plant is indigenous to the Orient and southern Russia, Levant wormseed (as the buds are termed) being the most highly valued. The principal constituent of wormseed is the well-known drug santonin, the well-known anthelmintic. The greater part, if not the whole, of the oil found in commerce is obtained from the santonin factories, and is said to differ slightly from the oil distilled from the seeds without extracting the santonin; this however is very doubtful. The yield of oil is about 2 per cent. It is a thick yellow to brownish oil of specific gravity ·930 to ·935, which is easily rendered colourless by rectification. This oil has been the subject of numerous researches, the results obtained being extremely variable, no doubt due to difference in the species of *Artemisia* used, or to the employment of adulterated oil. Völckel (*Annalen*, lxxxvii., p. 312) stated that it was a mixture of bodies to which he assigned the names cinæbene and cinæbene camphor, without giving any very definite evidence of their purity. Kraut and Wahlfors (*Annalen*, cxxviii., p. 293) found the chief constituent of the oil to be a substance of the formula $C_{10}H_{18}O$. This body is clearly cineol, which is

definitely settled as the principal constituent of the oil. Faust and Homeyer (*Jour. Chem. Soc.*, 1875, p. 371) assigned to the principal constituent the formula $C_{10}H_{16}O$. Hell and Stürcke (*Berichte*, xvii., p. 1970), using the oil from *Artemisia vahliana*, one of the species contributing to the Levant wormseed, confirmed the presence of cineol $C_{10}H_{18}O$. The presence of cineol was again confirmed by Wallach and Brass (*Annalen*, ccxxv., p. 291), who also obtained a terpene from the oil, which is probably dipentene. Another oxygenated body is also present, which may be a compound containing propionic acid, but it has not yet been isolated.

Artemisia Barrelieri yields an essential oil of specific gravity about ·920 which contains thujone. *Artemisia glacialis*, the "mountain wormwood," known commercially as "Genepi des Alpes," yields under ½ per cent. of an oil of specific gravity ·964 to ·970, which solidifies to a buttery consistency at 0°. It has been suggested as a suitable ingredient for making liqueurs to imitate the famous Benedictine and Chartreuse. *Artemisia vulgaris* yields the so-called *mugwort oil*, a liquid of specific gravity ·905 to ·910, containing cineol. *Artemisia abrotanum* is the *southernwood* or *old man* of our gardens, which yields small quantities of a fragrant essential oil. *Estragon oil* or *tarragon oil* is the product of *Artemisia dracunculus*. This plant is a native of Siberia and is cultivated in Europe. The yield of oil from the fresh herb varies from ·1 to ·4 per cent., and from the dried herb from ·2 to ·8 per cent. Messrs. Schimmel & Co. have cultivated this herb at their Miltitz plantations, and give the following figures for three samples of their own distillation :—

	Specific Gravity.	*Rotation.*
1.	·923	+ 5° 15′
2.	·932	+ 8° 10′
3.	·906	+ 5° 45′

The limits may be taken as ·890 to ·960, and for the rotation from + 2° to + 9°. The odour of this oil, recalling that of anise, led to the statement that anethol was a constituent of the oil. Grimaux and Schimmel are agreed that this is not so, but that the chief constituent is methyl-chavicol (estragol).

This oil is used in the manufacture of various sauces, vinegars and other culinary preparations. It is worth about 40s. per lb.

Tansy Oil.—This oil is distilled from the herb *Tanacetum vulgare*, a native of England, but cultivated in France, Germany, the United States, etc. The yield of oil from the fresh herb is about ·1 to ·2 per cent., and from the dried herb about twice this quantity. The specific gravity varies from ·925 to ·950. The rotation of the English oil is about – 25° to – 35°, whilst the foreign oil is dextro-rotary from + 30° to + 45°. The earliest thorough examination of this oil was made by Bruylants (*Berichte*, xi., p. 450), who stated that it contained an aldehyde $C_{10}H_{16}O$, which he called tanacetylhydrine. Semmler examined this body and showed that it was a ketone, and renamed it tanacetone. Wallach has shown, however, that it is identical with the ketone of thuja oil which he had already named thujone. Schimmel & Co. showed that the oil contains traces of borneol and some *laevo*-camphor, a fact indicated by Persoz previously (*Comptes Rendus*, xiii., p. 436). The English oil, which is strongly laevo-rotary, also contains much more camphor than the ordinary American oil. A sample distilled by Sawyer and examined by Schimmel & Co., deposited a considerable amount of camphor when cooled to 0°.

The oil is useful for perfuming toilet preparations, a reliable American oil being worth about 17s. per lb.

Tanacetum balsamita yields about ·07 per cent. of essential oil. According to Schimmel & Co., a sample

distilled by themselves had a specific gravity ·943, optical rotation $-53° 48'$, and a saponification number equal to 2·1 per cent. of KOH. On standing in a cold place crystals of a paraffin-like substance were deposited. The oil is not soluble in twice its volume of 80 per cent. alcohol, but is in the same quantity of 90 per cent. alcohol. The oil distilled completely between 207° and 283°, and gave the following fractions :—

207°-220° = 10·4 per cent.		240°-250° = 12·4 per cent.	
220°-230° = 16·8	,,	250°-283° = 21·2	,,
230°-240° = 18	,,	Residue = 21·2	,,

Achillea coronopifolia, according to Willdenow, yields an oil of deep blue colour and specific gravity ·924, with a strong odour of tansy. *Achillea moschata* yields the so-called *Iva oil*, of specific gravity ·932. This is a light blue oil containing cineol. *Achillea millefolium* also yields ·07 to ·13 per cent. of oil, the so-called milfoil oil, of specific gravity ·905 to ·925. This also contains cineol, and a very large amount of the blue colouring matter, so characteristic of this series of oils. *Achillea nobilis* and *Achillea ageratum* are also said to be used in the preparation of milfoil oil.

Arnica Oil.—Both the flowers and the root of *Arnica montana* yield essential oils, the former to the extent of about ·1 per cent., the latter up to 1 per cent. The plant is indigenous to Europe, growing upon the Swiss and German mountains, and the more northern plains. It is also met with in northern Asia and the south-western parts of America. The root oil, which is only worth about one-tenth as much as the rarer flower oil, is slightly laevo-rotary, about $-2°$, and has a specific gravity from ·990 to 1·000. The chemistry of this oil has been investigated and the following bodies have been identified : phlorone isobutyric ether $C_8H_8(OC_4H_9)_2$, thymohydroquinone dimethyl ether, $C_{10}H_{12}(OCH_3)_2$, and phlorone dimethyl ether $C_8H_8(OCH_3)_2$.

The flower oil is a blue to bluish-green oil when fresh, turning yellow or brown on keeping. Its specific gravity is ·905 to ·910. When exposed to cold it becomes solid or semi-solid, owing to the presence of a paraffin hydrocarbon. Esters of lauric and palmitic acid are also present. These oils are only used to a small extent in medicine.

Carlina Oil.—This oil is distilled from the root of the thistle, *Carlina acaulis*, indigenous to Central Europe. It is a dark coloured oil of aromatic taste and odour, of specific gravity from 1·030 to 1·040. This oil has been examined chemically, but a careful inspection of the figures obtained shows that the results are not reliable. It is probable, however, that a sesquiterpene is present, together with several oxygenated bodies, one of which is a crystalline body.

Costus Oil.—The root of *Aplotaxis Lappa*, a plant indigenous to eastern India, yields about 1 per cent. of an oil with a characteristic odour recalling that of orris or violets. This plant named as above by Decaisne is identical with *Aplotaxis auriculata* (De Candolle), *Aucklandia Costus* (Falconer), and *Saussurea hypoleuca* (Sprengel). It grows at elevations of 7000 to 12,000 feet on the north-western Himalayas, being found freely as far east as Sikkim and as far west as Kashmir and Lahore. The oil is of a light yellow colour, of specific gravity from ·980 to ·987 and optical rotation from + 15° to + 16°. It commences to boil at 275°, and about half distils over below 315°, when decomposition takes place. On keeping the oil develops an unpleasant odour, which, however, Messrs. Schimmel & Co. claim to remove by a special process which they do not divulge. The oil is employed in fine perfumery, being worth about £10 per lb.

Dog Fennel Oil is obtained from the entire plant *Eupatorium fœniculaceum*, which is widely distributed throughout North and South America. The oil has a light

yellow colour and a pepper-like odour, not at all resembling true fennel oil. The specific gravity is about ·935 and the rotation about + 18°. It contains a large amount of phellandrene.

Goldenrod Oil.—The oil usually known under this name is that obtained from the "sweet scented golden rod" *Solidago odora*, a plant very common in the United States east of the Rocky Mountains. Canadian goldenrod oil, however, is yielded by *Solidago canadensis*, of which a sample of authentic origin had a specific gravity ·859 and a rotation − 11° 10′. This is one of the other species closely resembling *Solidago odora*, of which over forty are found in the United States. The oil contains 85 per cent. of terpenes, as its low specific gravity indicates, which consist chiefly of pinene, together with phellandrene and dipentene, with probably some limonene. Borneol (10 per cent.), bornyl acetate (4 per cent.), and cadinene are also present. *Solidago rugosa* also yields an oil, but it possesses an odour recalling *Origanum* and differs from that above described. The oil from *Solidago odora* has not been thoroughly examined, but it contains much less terpenes than the oil from *Solidago canadensis*.

Fleabane Oil.—This oil, also known as erigeron oil, is distilled from the fresh flowering herb, *Erigeron canadensis*, a plant widely distributed through North America, and known locally as horseweed, fleabane, butterweed, colt's tail, etc. Only about ½ per cent. of oil is obtained, and this is of a light yellow colour and aromatic odour. The pure oil has a specific gravity of ·850 to ·890, and an optical rotation of about + 50°. The known constituents of the oil are the terpene limonene and terpineol.

Elecampene Oil is distilled from the root of *Inula helenium*, which yields from 1 to 2 per cent. of oil. The plant is a native of southern Asia and Siberia, and is found

in southern Europe and North America. According to Marpmann (*Arch. Pharm.*, xxv., p. 826), the oil contains helenin C_6H_8O, alantic anhydride $C_{15}H_{20}O_2$, and alantol $C_{20}H_{32}O$. According to Keallen, the oil consists of a liquid portion, of the formula $C_{10}H_{16}O$, which he terms alantol, and a solid portion of the formula $C_{15}H_{22}O_2$, which is identical with Marpmann's alantic anhydride. According to Schimmel & Co., helenin is identical with alantic acid and has the formula $(C_6H_8O)_x$. The probable constituents of the oil are therefore alantic acid, alantic anhydride and alantol, all bodies whose chemical relationships require elucidation.

Helichrysum Oil is the product of distillation of the flowering herb, *Helichrysum Stœchas*. It is an oil of specific gravity ·873, and probably contains pinene.

Kiku Oil is distilled from the leaves of *Pyrethrum indicum*. It is a liquid of specific gravity about ·880 to ·890.

Ragweed Oil is a dark green oil distilled from the flowering herb *Ambrosia artemisifolia*, which yields under $\frac{1}{10}$ per cent. of oil. Its specific gravity is ·870, and optical rotation $-26°$.

N. O. CAPRIFOLIACEÆ.

Elder Oil is a product seldom seen in commerce. It has been obtained by distilling the fresh flowers with water and extracting the water with petroleum ether. It forms a greenish semi-solid mass with a penetrating odour. According to a very old investigation by Dr. Gladstone, it yields sulphuretted hydrogen when distilled without water, and contains a terpene and a crystalline solid.

POLYPETALÆ.

N. O. UMBELLIFERÆ.

It will be convenient to discuss here two oils yielded by the N. O. *Magnoliaceæ*, on account of their connection with aniseed oil.

Aniseed Oil.—Two varieties of aniseed oil, almost identical in composition and properties, are known in commerce. Of these one is derived from *Pimpinella anisum*, the true anise, belonging to the natural order *Umbelliferæ*, and the other, which constitutes the bulk of the commercial oil, from *Illicium verum*, the star anise, one of the *Magnoliaceæ*.

Pimpinella anisum is indigenous to Asia Minor and Egypt, and is also cultivated in Russia, Spain, Malta, Greece, Bulgaria, Chili, India and several other parts of Europe. Russia produces the greater part of the anise fruit used for distillation, after which Asia Minor comes chiefly into consideration. The exports during 1896 from these countries and from Spain were as follows:—

Russia	1,118,600 kilos.
Levant	400,000 ,,
Spain	126,200 ,,

The total production is, of course, much greater; that, for example, in Spain, having reached nearly one million kilos in 1898. In Russia, from which country most of the fruit used for distillation is obtained, farmers in the districts of Walcysk, Birjutschensk and Ostrog, and to a less extent Podolia, Kursk, Charkow, Tauria and Cherson, cultivate the plant, a portion of the fruit being distilled on the spot, or used for domestic purposes, the remainder being exported. The commercial centres of the anise trade are Krassnaja and Alexejewskaja.

The star anise (*Badiane*) is chiefly found in southern China and Tonkin. The earliest reliable information as to the actual habitat of this plant was furnished by Mr. Piry in his report on the trade at Pakhoo for the years 1878-79, in which he states that the fruit is brought for export to Kin Chow and Pakhoi from Kwang-Si, chiefly from Lung-chow on the borders of Annam, and Po-sé on the West

River close to Yunnan. The oil is chiefly distilled by the natives, and sold to merchants who transfer it to Hong-Kong, where it is bought by the exporters and sent to Europe, very frequently in a grossly adulterated condition. According to Simon, the adulteration is practised not by the distillers, but by the "Bande Noir," as he terms the Chinese merchants who combine to buy the oil from the native distillers, keeping them more or less under their dominion, by means of money advances in the early part of the season. European merchants, however, now have their agents both in the Kwang-si and Tonkin districts, who collect the oil immediately it is distilled and transport it either to Hong-Kong, Pakhoi or Haiphong, from where it is shipped to Europe. The greatest care is necessary in purchasing this oil on account of the heavy adulteration, especially with petroleum, practised by the Orientals. In Annam the process of distillation is as follows. About 20 lb. of the fruit are placed in an iron pan and covered with water. Upon this is placed, bottom upwards, so as to form a cover, a second iron pan pierced with a circular opening, over which is placed an earthen vessel with three small orifices in the lower part, which allow the access of vapour into this vessel. These orifices are covered on the inside by small ear-shaped hoods which cause the vapour to be spread over to the sides of the vessel. This earthen vessel is covered with an iron pan, which performs the part of a refrigerator, and into which a continuous current of cold water is admitted. The joints of the first two iron pans are luted and the earthen vessel and the refrigerator are jointed with rag bandages. The vapour reaches the earthen vessel and is condensed when it strikes the bottom of the refrigerator, and falls into a circular trough at the bottom of the vessel, whence it escapes through a small pipe. The average annual production of oil is as follows:—

District of Po-Sé	90,000 kilos.
District of Lung-chow	30,000 ,,
District of Lang-So	30,000 ,,

The yield obtained is from 2·5 to 5 per cent. In Europe the oil distilled from the following growths of *true* anise yielded the following results (Schimmel):—

Chilian	1·9 to 2·6	Italian	2·7 to 3·5
Macedonian	2·2	Moravian	2·4 to 3·2
Mexican	1·9 to 2·1	East Prussian	2·4
Russian	2·4 to 3·2	Spanish	3·0
Syrian	1·5 to 6·0	Thuringian	2·4

Aniseed oil is a pale yellow oil of syrupy consistence, solid below about 15°. Its specific gravity is ·980 to ·990, and it is usually slightly laevo-rotary 0° to −2°, but never dextro-rotary. (Squire has reported some dextro-rotary oils, but they were probably adulterated with fennel oil.) In these, as in other physical properties, no difference of importance exists between the two oils. The *British Pharmacopœia* allows ·975 to ·990 as the limit of specific gravity when taken at 20°—presumably meaning $\frac{d^{20°}}{d^{15°}}$. As it is not easy to keep the oil liquid at 15·5° in certain cases, the gravity may well be taken at the higher temperature. The usual adulterants are petroleum, fennel oil, or its stearoptene, and the waste liquid portion of the oil obtained in the manufacture of anethol (the solid odorous constituent of the oil). In addition, spermaceti has been said to be added, but the author has never met with a sample adulterated with this body. The value of the oil depends on the quantity of anethol it contains, and as this melts at 21° and boils at 232°, the melting point and the behaviour on fractionation of the oil yield most valuable information as to its purity. With regard to the latter, the fraction obtained between 225° and 235° should not be less than 80 per cent.—usually varying from 80 to 85 per cent.—corresponding to practically that quantity of anethol.

Anethol has a great tendency to exist in a state of superfusion, so that the oil can be easily cooled down, if not agitated, below its normal solidifying point, consequently it is necessary either to solidify the oil in a very thin test-tube, and take its melting point, or to determine its solidifying point in Beckmann's apparatus, which is illustrated on page 88. Schimmel & Co. describe the method they adopt in the following terms, and the author considers it yields very concordant results :—

" For the determination of the point of solidification of essential oils, the well-known Beckmann's apparatus for the determination of the molecular weight from the decrease of the freezing point may well be used. A few small modifications make it particularly suited for the examination of anise- and star-anise oils. These slight alterations consist mainly in the removal of the cork-connections, by which the *full view of the mercurial column of the thermometer is* impeded. The lateral branch of the freezing tube, C, of the Beckmann's apparatus, serving for the introduction of the substance to be examined, can also be omitted. The illustration (see page 88) explains the apparatus as modified by us for our purpose. The battery jar, A, serves for receiving the refrigerating fluid. The test tube, B, suspended in the metal cover serves as aircover around the freezing tube, C, preventing the premature solidification of the oil to be examined. This tube is wider at its top, narrowing down at the junction where it rests on the rim of the lower tube, B. In order to support the tube C in the tube B, three glass protuberances are affixed on its inside about 5 c.c. below its upper rim. The thermometer, divided into ½ degrees, is supported in a metallic cover by three small springs, permitting a ready displacement both upwards and downwards.

" For making the determination for anise- and star-anise oils, the jar is filled with iced water and broken ice, for fennel

oil with a freezing mixture consisting of broken ice and common salt. Then the sample of oil to be tested is introduced into the freezing tube, C, reaching to a height of about 5 cm., and the thermometer is inserted into the oil with the precaution not to touch the wall of the tube in any place. During the cooling process any concussions have to be avoided, as they tend to cause a premature solidification of the oil. When the thermometer has reached about 10° below the point of solidification, this being at 6° to 8° for anise- and star-anise oils, the solidification is induced by gentle friction with the thermometer upon the wall of the tube holding the oil. Should this simple procedure fail in its object, a minute crystal of solidified oil or of anethol may be introduced into the fluid, whereupon the crystallisation sets in at once, disengaging considerable heat. It may be accelerated by constantly stirring with the thermometer, whose mercurial column rapidly rises, soon reaching the maximum height, called the solidification point of the oil."

The solidification point taken in this way, or the melting point, should not be below 15°. It usually varies in pure samples between 16° and 18°, according to the percentage of anethol. Small quantities of petroleum do not bring this point below the lowest limit for a pure oil, but even 2 or 3 per cent. greatly interferes with the solubility in alcohol. The pure oil is soluble in three volumes at most of 90 per cent. alcohol, whereas an oil adulterated with 5 per cent. of petroleum will not dissolve in ten volumes. On keeping for any considerable time, the oil becomes partially oxidised, with the formation of anisic aldehyde and anisic acid, with a lowering of the melting point and raising of the specific gravity. Within the last year or two some samples of aniseed oil appeared on the German and London markets, which possessed an abnormally low melting point. No adulterant could be detected in these, although the melting point varied

from 8° to 11°. Two views have been taken on this point. Umney has examined a sample of star-anise leaf oil, which, according to Simon, is largely distilled in the Po-Sé district. He finds its specific gravity to be ·9878, its rotation + 1°, and its solidification point below that of the ordinary fruit oil. A larger percentage of anisic aldehyde was also indicated by its behaviour on fractionation, and towards the usual aldehydic reagent—fuchsine decolourised by sulphurous acid. Possibly the oil in question was distilled from leaves and fruits. The other view, which the author supports, is that the flowers, or very early fruits, are distilled and yield an oil with a much lower anethol content. It is believed that some of the flowers or very young fruits are removed in order to allow the remainder to develop to the best advantage, and instead of being thrown away, these are distilled. Some oil from Tonkin, said to be oil of this description, absolutely free from petroleum and apparently quite authentic, gave the following results :—

Specific gravity	·9916.
Rotation	+ 0° 23′.
Solidifying point	12°.

A pure commercial oil, however, should certainly solidify not below 15°, should have a specific gravity ·975 to ·990 and an optical rotation 0° to − 2°, and not less than 80 per cent. should distil between 225° and 235°.

Although the physical characters of the true aniseed and the star-aniseed oil are practically identical, the constituents other than anethol, so far identified, are not quite so. Anethol, methyl-chavicol, and traces of anisic aldehyde and anisic acid are so far the only constituents which have been identified with certainty in the oil of *Pimpinella anisum.* Bouchardat and Tardy stated (*Comptes Rendus,* 1896, p. 198) that they found fenchone and anisic ketone $C_{10}H_{12}O_2$ in the oil, but as the sample upon which they worked was dextro-rotary and

melted at 10°, it was probably adulterated with fennel oil, and the results are valueless. In star-aniseed oil, anethol, methyl-chavicol, anisic aldehyde and anisic acid (in traces), dextro-pinene, laevo-phellandrene, and the ethyl ether of hydroquinone, and probably safrol, have been detected. According to Tilden, a dextro-rotary terpene is present in *both* oils. The two oils may be detected by the following test: a saturated solution of hydrochloric acid gas is added to the oil, and gives a rich blue colour with anise, and a yellow or brown with star-anise oil.

The fruit of a plant, *Seseli Harveyanum*, known in Victoria (Australia) as aniseed, but which more closely resembles fennel, yields an oil which has been examined by Umney, who found its specific gravity to be ·914 and its rotation + 14°. It was still liquid at 4°. The oil thus resembles fennel more than anise oil.

A false aniseed, also belonging to the N. O. *Magnoliaceæ*, is found in Japan under the name "Shikimi no Ki". It is the *Illicium religiosum*, and its oil is known as Shikimi or Japanese star-anise oil. Eijkmann distilled 40 kilos of the leaves—which are usually employed for the preparation of the oil, although the fruit yields an oil—and obtained 177 grammes of oil. It was a strongly refractive, faintly yellow oil of specific gravity 1·006. It contains eugenol and safrol, and a terpene, probably limonene. The so-called anise bark oil, prepared by Schimmel & Co. from the bark of *Illicium parviflorum*, which yielded 3½ per cent., is an oil of spicy taste, and odour recalling sassafras and tarragon. It had a specific gravity ·969 and optical rotation − 0° 46′. It consisted chiefly of methyl chavicol, containing very little anethol.

Pure anethol, of melting point 21° to 22°, is now a commercial article, and is preferred by some to the natural oil. The oil is used in perfumery, in the preparation of cordials and liqueurs, and in pharmacy. Its price varies somewhat.

At the present moment Russian oil is worth about 8s., and star-aniseed oil about 7s. 6d. per lb.; anethol being worth about 1s. 6d. per lb. extra.

Caraway Oil. — This oil is distilled from the seed of *Carum carui*, a plant inhabiting the low-lying lands in many parts of northern and central Europe. It is cultivated in England, Germany, Holland, Prussia, Morocco, etc. The Dutch fruit is esteemed very highly, and the oil obtained from it is worth more than that obtained from any other, except English, which however is a matter of local sentiment. Schimmel & Co. give the following as the average yields obtained from various fruits :—

Bavaria, wild	6·5-7 per cent.
Finnish	5-6 ,,
Hessian, wild	6-7 ,,
Moravian, cultivated	4 ,,
East Frisian	5·5-6 ,,
Russian, wild	3·2-3·6 ,,
Styrian	6 ,,
Wurtemburg	5·5-6 ,,
German, cultivated	3·5-5 per cent.
Galician	4·5 ,,
Dutch, cultivated	4-6·5 ,,
Norwegian, wild	5-6·5 ,,
East Prussian, cultivated	5-5.5 ,,
Swedish, wild	4-6·5 ,,
Tyrolese	6·5 ,,

Caraway oil is one of those whose chemistry is almost fully understood. Normal caraway oil consists almost entirely of two components, the terpene, dextro-limonene, and carvone. Traces of carvacrol may also be present. The physical properties of the two chief constituents are well defined and very different, so that those of the oil give an approximate estimate of the percentage of the two bodies present. They are as follows :—

	Boiling Point.	*Specific Gravity.*	*Rotation.*
Limonene	175°-176°	·846	+ 107° (approx.)
Carvone	224°	·964	+ 62° ,,

Pure caraway oil possesses a specific gravity of ·910 to ·920 (pharmacopœial limits) and an optical rotation of + 70° to + 85°. Samples with a specific gravity below ·910 may occasionally be found, but in general they should be regarded

with suspicion, for if not adulterated, their natural carvone content is low. The valuable constituent of this oil is the carvone, and on this account, and as it is easy to separate this body in a fairly pure state, carvone is often used in place of the oil, and is official in the *German Pharmacopœia*. The result is that there is much de-carvonised oil on the market to be disposed of. A portion of the carvone is abstracted by fractional distillation, and the misleading name "rectified caraway oil" often given to the remaining oil, which frequently has a specific gravity of ·890 to ·900 and a correspondingly high rotation. When all the carvone is abstracted the resulting "carvene," as it is called—in reality almost pure limonene, with traces of carvone—is sold as "light" oil of caraway. It is used for perfuming cheap soaps, but it is false economy, as the same value in pure oil or in carvol has a far higher odour value, and is cheaper in the end. "Carvene" is comparable to "citrene," the waste terpenes obtained in preparing terpeneless oil of lemons, and "auranciene," the corresponding terpenes from orange oil. They are all practically useless for perfumery purposes, and are either sold under misleading names, or used to adulterate the respective oils from which they have been obtained. There is also an oil known as caraway chaff oil, which appears to be distilled from a mixture of the herb itself, and the chaff obtained on threshing the seeds. "Light" caraway oil examined by the author had a specific gravity ·848 and an optical rotation + 103°. Umney gives a sample of "light" caraway or "chaff" as having a specific gravity ·8482 and an optical rotation of − 58·5°. Attempting to determine the question as to when the carvone was formed in the plant, Messrs. Schimmel and Co. distilled the samples described below, grown by them on their Miltitz fields:—

No. 1 from fresh long-cut, blooming plants with partly ripening fruits.

No. 2 from fresh plants cut at the same time and in the same way, from which, however, the umbels bearing both flowers and ripening fruits had been removed, so that the stalks and the leaves alone were distilled.

No. 3 from plants in a more advanced stage of ripening, and after the time of blooming, but before the full ripening of the fruits.

The following were the physical constants of the oils obtained:—

	Specific Gravity.	*Refractive Index.*	*Optical Rotation.*
No. 1	0·882	1·48306	+ 65° 12′
,, 2 about	0·880	1·5083	+ 20° 36′
,, 3	0·9154	1·48825	+ 63° 6′

The odour of oil No. 2 hardly resembled that of caraway seeds, nor did it contain either limonene or carvone, the characteristic constituents of caraway oil, in any perceptible quantity. *The small sample was just sufficient* for ascertaining the boiling point; it began to boil at 195° C., the thermometer then rapidly rose to 230° C., and between 230° and 270° about 65 to 70 per cent. distilled over; the residue was resinified.

Sample No. 1 evidently contained much more terpene and less carvone than sample No. 3. Hence it is probable that the latter results from the oxidation of the former during the ripening of the plant. A body of high boiling point, not yet identified, was detected in small quantity in each of these oils.

The percentage of carvone being the criterion of the value of this oil, the analysis of it should be especially directed towards this point. A high carvone content is indicated by a high specific gravity and (comparatively) low rotation. These should vary between ·910 and ·920, and + 70° to + 85° respectively. On fractional distillation not more than 25 per cent. should distil below 185°, and at least

55 per cent. to 65 per cent. should distil over 200°, a considerable fraction—40 per cent. to 50 per cent.—being obtained from 220° to 230°.

Various direct methods of determining the carvone have been proposed, based on the preparation of crystalline compounds of this body (*q.v.*, p. 55). The oxime, the sulphuretted hydrogen compound and the phenylhydrazone have been employed, but only approximate results can be obtained in all these cases. The following are the details recommended in the case of the phenylhydrazone:—

When 5 c.c. phenylhydrazine are added to 5 c.c. of caraway oil the mixture becomes warm owing to chemical combination taking place, and if the action be accelerated by placing the test tube in boiling water for a few minutes a copious crystallisation of carvone phenylhydrazone, $C_{10}H_{14} : N . NH . C_6H_5$, appears, and on cooling the whole solidifies to a crystalline mass. After heating for one hour the reaction is complete, the excess of phenylhydrazine is removed by adding 5 c.c. glacial acetic acid whilst hot, shaking and diluting with 20 c.c. water. The contents of the test tube are then cooled and filtered through a paper disc by means of a pump, and the crystalline mass washed with water until of a pale yellow colour. By this process not only is the excess of phenylhydrazine removed in aqueous solution as acetate, but nearly all the oily terpene adherent to the crystals is washed away. On crystallising from a definite volume of 95 per cent. alcohol the carvone phenylhydrazone is obtained in long silky pale yellow needles, melting at 106° C., but so difficult to dry, without decomposition as to render the determination only approximate.

Caraway oil is employed in the preparation of liqueurs, in perfumery and to a certain extent in pharmacy. The price is variable, but at the present moment it is worth about 5s. to 6s. per lb. (Dutch seed oil). The "light" oil is sold

about 1s. 6d. per lb., but is not worth so much from the perfumer's point of view.

Coriander Oil.—This oil is distilled from the fruit of *Coriandrum sativum*, a native of the Levant and southern Europe, cultivated in many places all over the world. The average yield from various fruits is given by Schimmel & Co. as follows:—

French .	·4 per cent.	Dutch .	·6 per cent.
Italian .	·5 ,,	Moravian	·8 ,,
Morocco .	·2 to ·3 per cent.	East Indian	·15 to ·2 per cent.
Russian .	·8 to ·1 ,,	Thuringian	·6 to ·8 ,,

Thuringia and Russia have, of late, been the most important producers, the crops from these districts sometimes reaching as high a figure as 450 tons. The oil has an intense odour of the seeds, which is much impaired if immature fruits have been used in the distillation. This is explained by the following experiment undertaken by Schimmel & Co. A portion of a crop was gathered in the early summer, whilst the herb was in early flower, and the whole herb distilled. Five weeks later, when half ripe and just starting to seed, another portion was gathered and distilled. In another month, the fully ripe fruit of a third portion was distilled. The result of the examination of the oils obtained is given below in Messrs. Schimmel & Co.'s own somewhat expressive language:—

"1. *Oil from the entire Flowering Plant in the Green State.*—Yield 0·12 per cent. Sp. gr. 0·853. Insoluble in 70 per cent. alcohol. Extremely objectionable, bug-like odour. After $2\frac{1}{2}$ months the specific gravity of the oil had increased to 0·856. The optical rotation (which had not been determined immediately after distillation) was then + 1° 2′ in a 100 mm. tube at 18° C. The bug-odour had disappeared almost entirely. It would therefore seem that in the meantime the carrier of the odoriferous principle had become polymerised or otherwise transformed.

"2. *Oil from Green Half-ripe Coriander Herb, with Fruit.* —Yield 0·17 per cent. Sp. gr. 0·866. Optical rotation + 7° 10′ at 18°. Soluble in three parts of 70 per cent. alcohol. Odour resembling that of coriander, with a subsidiary odour reminding of bugs. After one month the specific gravity had increased to 0·869.

"3. *Oil from Ripe Coriander Fruit, distilled immediately after harvesting.*—Yield 0·83 per cent. Sp. gr. 0·876. Optical rotation + 10° 48′ at 16°. Soluble in three parts of 70 per cent. alcohol. Pure coriander odour."

The pure oil has a specific gravity ·870 to ·880, rarely to ·885 (the *B. P.* allows ·870 to ·885). Its optical rotation varies from + 8° to + 14°, rarely falling as low as + 7°. It should dissolve completely in three times its volume of 70 per cent. alcohol. On fractional distillation from 45 to 55 per cent. should be obtained between 190° and 200°, indicating a due proportion of linalol. The most common adulterant of this oil is sweet orange oil, which is detected by the lowering of the specific gravity and the increase in the rotation of the oil. The solubility is also interfered with. Oils of cubebs, cedar and turpentine are also occasionally added.

Semmler (*Berichte*, 1891, p. 206) isolated the characteristic component of this oil, which he termed coriandrol, an alcohol of the formula $C_{10}H_{17}OH$. Barbier has, however, shown that this is identical with *dextro*-linalol (*Comptes Rendus*, 1893, p. 1459). The only other known constituent of the oil is pinene.

Dill Oil is obtained by the distillation of the fruit of *Anethum graveolens*, Linnæus (*Peucedanum graveolens*, Bentham). It is indigenous to central and southern Europe, but is found in many other localities, such as the Caucasus, Persia and the north-east of Africa and India. Slight botanical differences exist between the European plant and that grown in India, so that the latter has been described

as a distinct species (*Anethum Sowa*). A difference of opinion exists as to whether this distinction is justifiable, but the oils obtained from the two plants are certainly not identical. The yield of oil obtained from the seeds is about 3 to 4 per cent. The oil (from the European plant) is a pale yellow liquid, of specific gravity about ·905 to ·920 (pharmacopœial limits), although Schimmel & Co. give oils they have distilled themselves with as low a gravity as ·899. This however must be regarded as very exceptional, and a specific gravity below ·905 is generally indicative of the abstraction of carvone. The optical rotation is from + 70° to + 80°. In spite of the difference in odour between this and caraway oils, the composition of the two is almost identical, both consisting nearly entirely of limonene and carvone. Dill oil however contains less carvone than caraway oil. Hence the tests given under caraway oil apply here, and stress should be laid on the specific gravity, optical rotation and fractionation. Not more than 15 per cent. should distil below 185°, and not less than 40 per cent. above 220°. English distilled oils usually have the highest specific gravity, from ·910 to ·916, and are consequently held in the highest esteem. The following are the average fractions obtained from English and German oils :—

	English.	*German.*
Below 185°	10 per cent.	10 per cent.
185°-200°	20 ,,	22 ,,
200°-220°	20 ,,	22 ,,
220°-230°	48 ,,	42 ,,
Above 230°	2 ,,	4 ,,

East Indian dill has a much higher specific gravity than European oil, this figure usually varying from ·945 to ·970. This high specific gravity is in all probability due to the presence of dill apiol, a body isomeric with ordinary parsley apiol, discovered by Ciamician and Silber. Indian oil contains much less carvone than European oil, as does the Japanese oil, which also possesses a high specific gravity and appears

to be nearly identical with Indian oil. The optical rotation of both varies from + 40° to 50°. Spanish oil also has a low rotation, from + 50° to + 60°. Schimmel & Co. claim to have found a large amount of phellandrene in a sample of English and also in Spanish oil. Apart from this, the only known constituents are limonene and carvone, with traces of a solid body, possibly a paraffin hydrocarbon, and, in Indian oil, dill apiol $C_{12}H_{14}O_4$. Pure dill oil is worth about 14s. per lb., and is used to a considerable extent in pharmacy as a carminative.

Fennel Oil.—This oil is distilled from the fruit of several varieties of *Foeniculum vulgare*, which is found all over Europe except in the north and north-east, being especially common on the Mediterranean littoral, and is also found in Asia Minor, Persia, India and Japan. Two oils are recognised in commerce, the "sweet" and "bitter" oils, the former being more esteemed. The sweet fennel is said to be *Foeniculum sativum*, but this is probably only a variety of the common wild fennel. The yield of oil obtained is very variable, according to the fruit distilled. In general it averages from 2·5 to 4 per cent. In the ordinary way, Galicia and Roumania furnish some of the best fennel crops, and from their fruit a large portion of the oil of commerce is distilled. The great variability in the fruits of different districts makes it necessary to fix some limits for the physical characters of the oil, which, however, may be exceeded in individual cases. The terpenes, pinene, phellandrene, dipentene and limonene, have all been detected in fennel oils, and the ketone fenchone and anethol. All these bodies, however, may not occur in any given sample. Upon the presence of anethol the value of the oil chiefly depends, and the solidifying point of the oil is therefore a fair criterion of its value, if the oil is pure. A good oil will contain as much as 60 per cent. of anethol. The specific gravity should

not fall below ·960 nor above ·980, and the optical rotation should vary from + 6° to + 20°. The solidifying point (*see Oil of Aniseed*) should not fall below + 5°. If necessary the crystalline stearoptene may be separated and examined, but as a rule added solid bodies will alter the other characters of the oil. The above tests will guard against the abstraction of anethol, or the addition of the residue of oil from which this body has been abstracted.

One observer gives as the specific gravity and optical rotation of the oil distilled from French bitter fennel, ·910 to ·955 and + 22° to + 48° respectively. Tardy, however (*Bull. Soc. Chim.*, xvii., p. 660), has examined a sample of this oil, and states that its specific gravity is 1·007 at 0°, and its optical rotation + 18° 20′. In the oil he found pinene, dipentene, cymene, phellandrene (?), *d*-fenchone, methyl-chavicol and anethol, together with anise aldehyde and anisic acid, and a ketone of the constitution—

$$C_6H_4\begin{cases}OCH_3\\CH_2.CO.CH_3.\end{cases}$$

Schimmel & Co. have examined a sample of Japanese oil, and give the specific gravity as ·9754, and the optical rotation as + 10° 3′. Umney gives ·9754 and + 15° 5′ for a sample of the same oil. He found 10·2 per cent. of fenchone in the oil.

Foeniculum piperitum yields an oil (*Sicilian fennel oil*) of specific gravity about ·950. Water fennel oil is obtained from the plant *Phellandrium aquaticum* (*Oenanthe phellandrium*), the fruit of which yields from 1 to 2 per cent. of oil of specific gravity ·860 to ·890. The chief constituent of the oil is the terpene phellandrene, but other constituents are certainly present, although not yet identified.

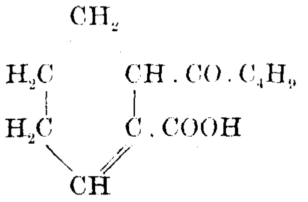
Cumin Oil or *Cummin Oil* is obtained from the fruit of *Cuminum cyminum*, a native of Upper Egypt and Ethiopia,

but cultivated in Arabia, India, China, Malta, Sicily, etc. The bulk of the supply of commerce is obtained from Sicily, Malta, Mogador and India. The yield is from 2·5 per cent. to 4 per cent. of a light yellow oil of specific gravity ·890 to ·930 and optical rotation + 4° to + 6°. The known constituents of this oil are cymene and cumic aldehyde. Wolpian (*Pharm. Zeit. für Russland*, 1896, p. 97) states that he has obtained from cumin oil a fraction boiling at 157° to 158°, which was a terpene which he could not identify with any known terpene. However, it is doubtful whether he obtained it in a state of purity, and the proposed name hydrocuminene appears rather premature, as no derivatives were prepared. The oil, which is worth about 13s. per lb., is not used very extensively.

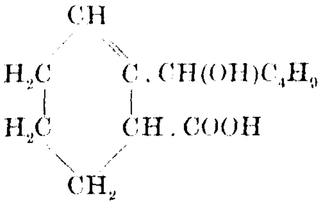
Oil of Lovage.—The ordinary oil of lovage is obtained by distilling the roots of *Levisticum officinale* with steam, the yield being under 1 per cent. The oil is a somewhat dark brown viscous liquid of specific gravity 1·005 to 1·045, and optical rotation from + 2° to + 7°. Braun (*Arch. Pharm.*, 1897, iii., p. 1) has investigated it, but he did not succeed in characterising any single constituent of the oil. Schimmel & Co. have detected terpineol in it, but, so far, the other constituents are unknown. The fresh herb also yields from ·1 to ·2 per cent. of an oil of specific gravity ·920 to ·925 and optical rotation + 35° to + 45°. The fruit yields 1 to 2 per cent. of an oil of specific gravity ·930 to ·940. Lovage oil is chiefly employed in liqueur and cordial making.

Celery Oil.—All parts of the herb *Apium graveolens*, the common celery, yield an essential oil, of which that from the seeds is most valued. Schimmel & Co., however, state that that from the green leaves most exactly reproduces the natural celery flavour. The oil from the seed is obtained to the extent of about 3 per cent., as a liquid of strong celery odour, having a specific gravity ·870 to ·895 and an optical rotation

+ 65° to + 80°. The chief constituent of the oil is dextro-limonene. Ciamician and Silber have recently (*Berichte*, 1897, p. 492) examined the high boiling fractions of the oil and found therein traces of palmitic acid, guaiacol and a crystalline substance of the formula $C_{16}H_{20}O_3$, melting at 66° to 67°. In addition, a sesquiterpene was found, and two bodies, both acids, of a peculiar constitution, sedanolic and sedanonic acids, together with the lactone of the former, sedanolide, which appears to be the chief odorous constituent of the oil. Sedanolic acid $C_{12}H_{20}O_3$ is a crystalline body melting at 88° to 89°, and is easily converted into its lactone sedanolide $C_{12}H_{18}O_2$. Sedanonic acid $C_{12}H_{18}O_3$ melts at 113°, and possibly occurs as an anhydride in the oil. These two acids are nearly related, and Ciamician and Silber consider that sedanolic acid is *ortho*-oxyamyl-tetrahydrobenzoic acid, and that sedanonic acid is a related ketonic acid. The following formulæ thus express the relations of these bodies:—

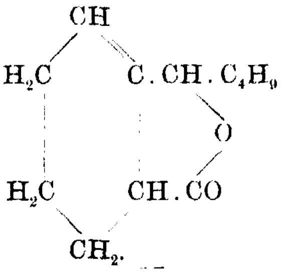


Sedanonic Acid.



Sedanolic Acid.

Sedanolide, the chief odorous constituent, would thus be tetrahydrobutyl-phthalide of the formula—



A closely related body, phthalylisopropylidene, and its reduction products, were prepared artificially and found to have an odour much resembling celery.

The green herb yields ·1 per cent. of an oil of specific gravity ·848 to ·855 and optical rotation + 45° to + 55°. Although it has not been thoroughly examined, it is probable that its constituents closely resemble those of the seed oil. The oil is soluble in ten parts of 90 per cent. alcohol.

Parsley Oil.—All parts of the common parsley, *Petroselinum sativum*, yield an essential oil, of which that from the green herb itself is most esteemed, although that from the seed is the commoner oil. The yield from the seeds is from 2 to 6 per cent. of an oil of specific gravity 1·050 to 1·100. It is *laevo*-rotary about − 5° to − 10°. The two well-ascertained constituents are pinene and apiol. If the oil contains more than a certain quantity of the latter body it is semi-solid at ordinary temperatures, whilst in any case crystals are deposited on exposure to cold. Apiol is prepared from the oil either as a thick liquid, or in the purer crystalline condition, and is used to a small extent in medicine.

The oils from the fresh herb and root resemble that from the seed, but are usually *dextro*-rotary. Further, the herb oil has a specific gravity as low as ·925.

Ajowan oil is the product of distillation of the fruit of the herb *Ptychotis Ajowan* (*Carum Ajowan*), a plant cultivated in many parts of Egypt, Persia, Afghanistan and Bengal. The fruit yields from 3 to 4 per cent. of oil of specific gravity ·900 to ·930, with a small dextro-rotation. The characteristic odour of the oil is due to the presence of from 40 to 50 per cent. of thymol. In addition, cymene and probably a terpene are present. The oil itself is used to a certain extent in India for medicinal purposes, but its principal use is for the preparation of thymol. According to Stohmann, carvacrol is also present, but this statement requires confirmation.

Angelica Oil.—All parts of the herb *Angelica officinalis* (*Angelica Archangelica*) yield essential oils, of which the best known is that distilled from the fresh root. The plant is a native of Europe, on mountains or river sides, especially in Lapland, Sweden, Norway, Germany, etc. It is cultivated to a considerable extent in Saxony, but is comparatively rare in Britain. Although the root oil is that mostly used, and held in high esteem, according to Schimmel & Co. the seed oil is preferable to this. Angelica root oil is a light yellow or reddish limpid liquid of strong aromatic odour and pungent taste. The yield from roots grown in the Saxon Erzgebirge is about 1 per cent. of oil. The specific gravity varies from ·860 to ·905, that from the dried root usually having a higher specific gravity than that from the fresh root. The optical rotation varies from + 18° to + 30°, usually about + 25°. On long standing crystals are deposited, which according to Giordani have the composition $C_{32}H_{62}O_5$, and melt at 74° to 77°. Beilstein (*Berichte*, 1882, p. 1741) showed that the oil contains one or more terpenes; Naudin (*Berichte*, 1883, p. 1382) confirmed this, and Schimmel & Co. have showed that amongst the lower boiling fractions of the oil, dextro-phellandrene exists. Ciamician and Silber (*Berichte*, 1896, p. 1811) showed that the crystalline bodies (of which they separated two) existing in the oil were probably oxyacid anhydrides. Hydrocarbons, probably sesquiterpenes, were also found, which distilled at 240° to 270°, and oxypentadecylic acid $C_{15}H_{30}O_3$. Giordani also isolated methyl-ethyl-acetic acid from the oil. The oil obtained from the seeds, which yields about 1 per cent., has a specific gravity ·856 to ·890, and an optical rotation of + 10° to + 13°. It contains phellandrene, methyl-ethyl-acetic and oxymyristic acids. The oil distilled from the whole fresh herb has a specific gravity ·869 to ·890, and an optical rotation + 8° to + 25°. Japanese angelica root, from which an oil is distilled, is from *Angelica anomala* (*Angelica refracta*?).

The oil, which is obtained to the extent of ·1 to ·2 per cent. of the root used, has a specific gravity ·910 to ·915. At 10° it becomes thick, and at 0° it solidifies to a paste. The crystalline mass thus deposited consists mainly of a fatty acid melting at 62° to 63°. The oil distils over between 170° and 310°; the last fractions have a blue-green colour. This oil has a more acrid odour than the Saxon oil, but distinctly recalls musk, although this is to a great extent covered by the other and less pleasant odour of the oil. The chief employment for angelica oil is in liqueur making.

Carrot Oil.—The seed of the carrot, *Daucus carota*, yields from 1 to 1·5 per cent. of oil of specific gravity ·870 to ·930 and optical rotation − 13° to − 40°. The oil has a characteristic carrot odour and contains pinene and either terpineol or cineol, possibly a mixture of both. The characteristic body responsible for the odour of this oil has not yet been identified.

Ammoniacum Oil is the oil obtained by distilling the gum resin of *Dorema ammoniacum* with water. The yield of oil is very small, usually about ·3 per cent. The oil has a specific gravity of about ·890, and is slightly dextro-rotary. It distils between 250° and 290°. Its composition is not known.

Asafoetida Oil.—The gum resin of certain species of *Ferula*, chiefly, in all probability, *Ferula Narthex* and *Ferula scorodosma*, both perennial herbs, indigenous to Turkestan, Bokhara, western Afghanistan and Cashmir, yields, when distilled with water, about 3 to 4 per cent. of a somewhat foul smelling oil of specific gravity ·975 to ·990 and optical rotation about − 10°. Semmler has investigated this oil, having separated by fractional distillation under reduced pressure two terpenes, one of which was probably pinene, and a sesquiterpene, which had a lavender-like odour. The remainder of the oil consists chiefly of compounds containing sulphur. According to Brannt, the oil contains allyl sulphide and allyl disulphide, but Semmler denies this. Sulphur com-

pounds of the formulæ $C_7H_{14}S_2$, $C_{10}H_{20}S_2$, $C_8H_{16}S_2$, and $C_{10}H_{18}S_2$ were found, together with an oxygenated body of the formula $C_{10}H_{16}O$, or a multiple of this.

Galbanum Oil is the product of distillation of the gum-resin, *Peucedanum galbaniflum* and probably other species indigenous to Persia. From 12 to 24 per cent. of oil is obtained, which has a penetrating odour and sharp taste. Its specific gravity is ·910 to ·940, and its optical rotation from − 5° to + 20°. The only constituents yet identified are pinene and cadinene.

Opoponax Oil.—The oil distilled from opoponax resin, as used in perfumery to-day, is *not* the product of the umbelliferous plant *Opoponax Chironium.* It will be noticed later.

Heracleum Oil.—The ordinary heracleum oil is distilled from the fruit of *Heracleum sphondylium*, the cow parsnip. The yield is from 1 to 3 per cent. of an oil of specific gravity about ·860 to ·880, and slightly *dextro*-rotary. According to Zincke, it contains octyl alcohol $C_8H_{17}OH$ and its acetic ester $C_{10}H_{20}O_2$ and caproic ester $C_{14}H_{28}O_2$. According to Möslinger, ethyl butyrate is also present; and also the lauric acid ester of octyl alcohol, and some hexyl compounds in very small quantities. The oil of *Heracleum giganteum* has been examined by Gutzeit, and found to correspond closely with that just described.

Masterwort Oil is distilled from the root of *Imperatoria ostruthium*, a plant indigenous to the mountain regions of southern and central Europe. The root yields about 1 per cent. of oil of characteristic aromatic odour, which, according to Hirzel, contains bodies resembling terpene alcohols. Wagner states that angelic aldehyde is present. The oil has a specific gravity about ·875, and distils almost entirely between 170° and 190°.

Mew Oil is obtained from the root of *Meum athaman-*

ticum to the extent of about ¾ per cent. The oil has a specific gravity of just over 1·000, and distils between 170° and 300°.

Sumbul Oil or *Musk-root Oil* is obtained from the dried root of *Ferula sumbul*. The yield of oil is only from ·2 to ·4 per cent. Its specific gravity is ·950 to ·965. It has a distinct musk-like odour, and in India the root of *Dorema ammoniacum* is often substituted for it and used under the name of sumbul root (see ammoniacum oil).

Pastinac Oil is obtained from the fruit of *Pastinaca sativa*. The yield is 1·5 to 2·5 per cent. of an oil of specific gravity ·870 to ·890, with a faint laevo-rotation. It somewhat resembles heracleum oil, containing ethyl alcohol, and propionic and butyric acid esters of octyl alcohol.

Peucedanum Oil.—The root of *Peucedanum officinale* and the fruit of *Peucedanum grande* yield small quantities of oil, both of specific gravity about ·900 and optical rotation + 30° to + 35° or thereabouts.

Pimpinella Oil is obtained from the dried root of *Pimpinella saxifraga*. Its specific gravity is ·960. It has an agreeable parsley-like odour, and commences to boil at about 240°. Its constituents are not known.

Silaus Oil is the product of distillation of the fruit of *Silaus pratensis*. The yield is 1 to 1·5 per cent. of a slightly dextro-rotary oil of specific gravity ·980 to ·990.

N. O. Myrtaceæ.

Pimento Oil or *Allspice Oil* is distilled from the fruit of *Pimenta officinalis*, Linn. (*Eugenia pimenta*, De Candolle.) The plant, a handsome evergreen, is indigenous to the West Indies, being found especially on calcareous soil near the coast on the islands of Cuba, Hayti, Trinidad, Domingo, Antigua, the Leeward and Windward Islands, and in abundance in Jamaica. The berries are gathered in an unripe condition, as when ripe they are filled with a sweet pulp

lacking the characteristic aroma of the green berry. These unripe berries, dried in the sun, form the pimento of commerce, and Jamaica alone exports, chiefly from the port of Kingston, about £50,000 worth per annum. The fruit, which is about the size of a small pea or large peppercorn, has an aromatic odour somewhat recalling cinnamon, nutmeg and pepper, with a predominating odour of cloves. This explains the origin of the name allspice. It yields from 3 to 4½ per cent. of oil on distillation, of a dark reddish colour and of the same aromatic odour as the fruit. So far the only well-ascertained constituents are the phenol eugenol, and a sesquiterpene, whose exact nature is not yet known. The former is, of course, responsible for the clove-like odour of the oil, and the latter, together with, possibly, one or more as yet unknown constituents, modifies the characteristic odour of the oil. A certain amount of resin, due no doubt to the unstable nature of some of the constituents, is usually present. The actual amount of eugenol in the oil is best estimated by Thom's process (*see Oil of Cloves*), and the remarks made in the monograph on oil of cloves on this estimation, apply here. The specific gravity of the oil is, to an extent, an indication of the amount of eugenol present, and should vary between 1·040 and 1·055. The *British Pharmacopœia*, in which this oil is official, states that the specific gravity should not fall below 1·040. The oil is laevo-rotary, but never exceeds $-4°$, usually about $-2°$. It is easily soluble in 90 per cent. alcohol and in twice its volume of 70 per cent. alcohol. Eugenol boils at 247°, consequently the fraction 245° to 250° should be considerable—in genuine oils not below 60 per cent., usually 70 per cent. or over. The amount of eugenol, as estimated by Thom's process (*see Oil of Cloves*), should not be less than 65 per cent.; and the residue not absorbed by caustic potash solution should not exceed 25 per cent.

This oil is used almost entirely as a flavouring agent, and it may be noted that the odour of the pure oil imported into this country is quite as fine, if not finer, than that distilled here.

Oil of Cloves.—The clove tree is a beautiful evergreen, indigenous to the Molucca Islands. It is cultivated in several of the islands to the south of the Moluccas, and in Sumatra, Penang, Malacca, Madagascar, the Seychelles, Bourbon, Mauritius, the West Indies, Zanzibar, and Pemba, our chief supply coming from the two last-named islands. The tree is *Eugenia caryophyllata* (*Caryophyllus aromaticus*, Linn.), and most parts of the tree have a very aromatic odour. The spice we know as cloves consists of the dried unexpanded flower buds, which are used in the distillation of the oil. The flower stems are also used, but the oil, although of very similar character, is not of so fine an aroma. As a spice Penang cloves fetch the highest price, but Zanzibar cloves are highly esteemed in commerce; it must be remembered, however, that the majority of "Zanzibar" cloves in reality come from the adjacent island of Pemba. A sophistication sometimes practised on this article is the addition to the natural clove of spent cloves from which the oil has been distilled, the latter of course being quite valueless as a spice. Few plants yield so much essential oil as does the clove. Genuine buds seldom yield under 15 per cent., often as much as 18 or 19 per cent. The flower stems, however, only yield about 6 per cent.

The oil consists almost entirely of the phenol eugenol, and the sesquiterpene caryophyllene. Traces of methyl alcohol and furfurol, together with an aldehyde not identified, have been discovered by Schimmel, and Erdmann has found a small quantity (about 1 to 2 per cent.) of acetyl-eugenol and traces of a salicylic acid compound, probably in the form of eugenol acetyl-salicylate (*Journ. für Pr. Chem.*, 1897, p.

143). A small quantity of amyl-methyl-ketone $C_5H_{11}\cdot CO\cdot CH_3$ has also been found, and is probably the most important of the subsidiary constituents, as it possesses a particularly fruity odour, and when added to a mixture of eugenol and caryophyllene imparts to it a characteristic clove odour. Whilst these bodies undoubtedly have an influence on the odour of the oil, the important constituent is eugenol.

The high specific gravity is indicative of the high eugenol content, but the presence of the bodies above mentioned does not allow of the percentage of eugenol being exactly proportional to the specific gravity, as it would be if no other body but caryophyllene were present. The approximate proportions of the two chief constituents however may be judged by the fact that pure caryophyllene has a specific gravity of about ·908, whilst that of eugenol is 1·070. Pure clove oil (from buds) has a specific gravity, according to the *British Pharmacopœia*, of at least 1·050. The author has found a slightly lower gravity in an absolutely pure sample drawn by one of the most reputable drawers in England. 1·048 to 1·065 will be found to cover all genuine samples, except those, of course, which are specially rectified to ensure a higher eugenol content, when the specific gravity approaches 1·070. The oil is faintly laevo-rotary, but never exceeds $-1^\circ\ 30'$; usually it is under -1°. These characteristics, together with an estimation of the eugenol, are quite sufficient to control the purity of the oil. The method suggested by Umney gives useful approximate results, but is subject to a not inconsiderable error. This consists in shaking a known weight of the oil with a 10 per cent. aqueous solution of potassium hydroxide in a Hirschsohn flask, and allowing the unabsorbed portion to rise into the graduated neck. This is measured and its volume corrected by multiplying it by ·908—the specific gravity of the sesquiterpene—and the unabsorbed portion returned as caryophyllene, the difference

being reckoned as eugenol. The globules of uncombined hydrocarbons have a great tendency to stick round the top of the flask and require some "coaxing" to rise and agglomerate in the neck of the flask. Heat will accelerate and assist this however. But the source of error lies in the fact that the aqueous solution of potash and potassium eugenate dissolves some of the sesquiterpene, which is thus reckoned as eugenol, and a too high result is obtained. The process proposed by Thom, although more tedious, gives more exact results. This depends on the conversion of the eugenol into benzoyl-eugenol. The following are the details, which should be carefully observed in order to secure accurate results:—

About 5 grammes of clove oil are weighed into a beaker of about 150 c.c. capacity, 20 grammes of 15 per cent. sodium hydroxide solution added, and then 6 grammes benzoyl chloride. *On stirring, the solid mass of eugenol sodium salt at first* formed goes into solution again as it is converted into benzoic ester, with evolution of much heat. In the course of a few minutes the reaction ends, and on cooling a solid crystalline mass of benzoyl eugenol is obtained. To this, 50 c.c. water is added, and the whole warmed on a water bath until the ester is completely melted to an oil, well stirred, cooled, and the clear supernatant aqueous solution filtered off. The crystalline mass is again washed with two successive quantities of 50 c.c. water, and the resulting impure benzoyl eugenol is recrystallised from alcohol, due allowance being made for its solubility in that medium. 25 c.c. of hot alcohol (90 per cent. by weight strength) are poured through the filter employed in the previous washing operations, in order to dissolve any adherent crystals, into the beaker, and the whole warmed upon the water bath until complete solution is effected. The solution is then cooled to 17° C., and the crystalline precipitate thrown upon a small weighed filter

paper, filtered into a 25 c.c. cylinder, and washed with 90 per cent. alcohol until the filtrate exactly measures 25 c.c. The filter and crystals are then removed to a weighing bottle, dried at 100° C. until constant, and then weighed. . From the total weight the weights of the filter paper and of the weighing bottle are deducted, from which the benzoyl eugenol is calculated. To the latter weight 0·55 grammes are added, being the weight of pure benzoyl eugenol dissolved by 25 c.c. 90 per cent. alcohol at 17° C. as determined by experiment.

This final quantity gives the amount of benzoyl eugenol, from which the amount of eugenol is easily calculated, eugenol having the formula $C_{10}H_{12}O_2$, and benzoyl eugenol $C_{17}H_{16}O_3$, so that $\frac{164x}{268y} \times 100$ = the percentage of eugenol, if x equals the weight of benzoyl eugenol obtained, and y the weight of oil used in the estimation. Under these circumstances the eugenol content should not fall below 75 per cent., or if estimated by absorption with potash not below 82 per cent., usually from 85 to 90 per cent. As the boiling points of eugenol and caryophyllene are both high, no appreciable portion of the oil should distil below 245°, or even a few degrees higher. These tests will ensure the presence of a due proportion of eugenol, a point very necessary to take into account, because of the frequent abstraction of part of the eugenol, which is used in the manufacture of vanillin, or to sell as pure eugenol. Absence of turpentine or petroleum is further ensured by the ready solubility of the oil in 90 per cent. alcohol. The oil from clove stems does not appreciably differ in its chemical composition from the above although its aroma is less delicate and it contains rather less eugenol. The oil is used to a certain extent in pharmacy, but to a much larger extent in the preparation of liqueurs and in perfumery, and has a very large commercial importance.

Oil of Bay.—This oil is the product of distillation of the

leaves of *Pimenta acris* (*Eugenia acris*) and probably other closely allied species, plants flourishing in the West Indies. It is frequently described as being derived from *Myrcia acris*, but there is a doubt whether this is identical with *Pimenta acris*. The most prized oil comes from St. Thomas. The yield of oil obtained is from 2 to 3 per cent., and according to Markoe (*Pharm. Jour.* [3], viii., p. 1005) the oil comes over in two portions, firstly, a light oil which distils over rapidly, then a heavy oil distilling over more slowly. This of course means nothing more than that there are constituents of bay oil which have widely different boiling points. The fact that the *United States Pharmacopœia* of 1880 gave the specific gravity of bay oil as about 1·040, caused the heavier fractions to appear in commerce under that name. Pure normal distillates, however, have a specific gravity of ·965 to ·995, and oils with a higher specific gravity must be regarded as suspicious, being possibly adulterated with oil of cloves or oil of pimento. The oil is slightly laevo-rotary, but should not exceed − 2°. The percentage of phenols (*see Oil of Cloves*) is an important factor in the valuation of the oil. In a genuine oil this figure should not fall below 60 per cent. The *United States Pharmacopœia* provides the following test to guard against adulteration with oils of cloves and pimento: "If to three drops of the oil, contained in a small test tube, five drops of concentrated sulphuric acid be added, and, after the tube has been corked, the mixture be allowed to stand for half an hour, a resinous mass will be obtained. On adding to this mass 4 c.c. of diluted alcohol, vigorously shaking the mixture and gradually heating to the boiling point, the liquid should remain nearly colourless, and should not acquire a red or purplish-red colour."

Our knowledge of the chemistry of this oil is chiefly due to Mittmann (*Arch. Pharm.*, xxvii., p. 529), who first thoroughly investigated the oil, and to Power and Kleber, who cleared up

several points left in an obscure state by the first-named chemist. According to Mittmann, pinene and probably dipentene are present, together with the principal constituent eugenol, and its methyl ether. He also believed a diterpene to be present, but this was probably formed by polymerisation during the distillations he effected. Power and Kleber do not agree that either pinene or dipentene are present, but state that the only terpene is *laevo*-phellandrene. The oxygenated compounds which these chemists state they have identified are eugenol, methyl-eugenol, chavicol, methyl-chavicol and citral. In addition to this they found a hydrocarbon of the formula $C_{10}H_{16}$ with the abnormally low specific gravity ·802. This, as well as other considerations, exclude the probability of this hydrocarbon being a terpene, and the chemists above named term it myrcene, and regard it as an open-chain compound. Whether this is so or not, is not settled by any positive evidence.

The oil is sometimes adulterated with oils of cloves and pimento, which cause an increase in the specific gravity, and should be tested for as given above. Turpentine is also added at times. This alters the optical rotation and specific gravity, and if the oil be distilled in a small fractionating flask the bulk of the turpentine is obtained in the early fractions. Assuming that pinene is not present at all in oil of bay, turpentine may be detected by adding to, say, the first 10 per cent. distilled, an equal volume of amyl nitrite and two volumes of glacial acetic acid. The mixture is kept cold in ice and salt and a mixture of equal parts of glacial acetic acid, and hydrochloric acid is added drop by drop so long as a blue colour is developed. If pinene is present a white crystalline precipitate of pinene nitroso-chloride $C_{10}H_{16}NOCl$ is formed. 10 per cent. of turpentine can be detected with certainty in this way. The oil should also be easily soluble in 90 per cent. alcohol. This oil is largely employed in perfumery, especially

in the preparation of the favourite toilet article, bay rum. It must not be confounded with the oil of Californian bay.

Eucalyptus Oil.—The oils distilled from the leaves of the various species of this enormous genus of the *Myrtaceæ* are in many cases so dissimilar that the generic term, eucalyptus oil, is meaningless unless the species is quoted. Several species, however, yield oils which are very similar to each other, and on this basis the *British Pharmacopœia* describes as eucalyptus oil the product obtained from *Eucalyptus globulus* and other species, giving definite characters of the oil, the two chief of which are the presence of a due proportion of cineol (eucalyptol) and the absence of appreciable quantities of the terpene phellandrene. The great variability in the oil from different trees will make it convenient to deal with this oil, firstly with reference to pharmacopœial oil, and afterwards with especial reference to the characters of the oils from those trees which in many cases are in no way similar to "*Eucalyptus oil, British Pharmacopœia*". It is now pretty well settled that whatever medicinal value this oil has—and it has been, and still is, used to a very large extent as a prophylactic against influenza—is due to the presence of cineol, or, as it was originally known, eucalyptol. The *British Pharmacopœia*, 1885, had not entirely recognised this, and allowed oils to be used officially which might, and often did, contain very little eucalyptol. The 1898 *Pharmacopœia*, however, limits the specific gravity to ·910 to ·930, which ensures a high percentage of cineol, which has a specific gravity of ·930, the terpene phellandrene having a specific gravity of ·860, or thereabouts. The optical activity of the official oil is now limited to the extremes + 10° and − 10°, and as cineol is the optically inactive constituent of the oil, and the terpene is highly active, a due proportion of the former body is here again ensured. A positive test, however, is also given,

although in such loose and vague language that it would bear considerable improvement. Scammell, of Adelaide, recently patented a method for the preparation of pure cineol, dependent on the fact that this body forms a crystalline compound with phosphoric acid, which is decomposed by water, liberating the pure cineol. The *Pharmacopœia* requires that the oil shall become semi-solid when mixed with syrupy phosphoric acid. The presence of more than small quantities of phellandrene is guarded against by the well-known nitrite reaction, which is as follows: to 2 c.c. of the oil dissolved in 4 c.c. of glacial acetic acid, 3 c.c. of a saturated solution of sodium nitrite is added, with constant stirring, the oil being kept cold. The oil should remain liquid in the absence of phellandrene. Although none of these requirements in itself forms a direct quantitative control of the amount of cineol present, taken together they effectively prevent any oil which contains less than about 50 per cent. of cineol from being used officially. In the author's opinion the specific gravity limits are too stringent. He has examined a large number of eucalyptus oils with cineol contents of 45 to 52 per cent., which corresponded with the above requirements in every respect except that the specific gravity was ·906 to ·910. The lower limit might well have been fixed at ·905.

The quantitative determination of the cineol present is a matter of importance. The earlier attempts in this direction gave distinctly too low results. The chief method adopted was a series of fractionations, retaining all those fractions distilling between 173° and 190°, cooling them to − 15°, filtering off the still liquid portion, retaining the crystals of cineol, refractionating the liquid portions and again freezing, subsequently weighing the crystallised cineol. An average loss of about 10 per cent., in the author's opinion, takes place in this process, assuming the oil to contain 50 to 60 per

cent. of cineol. Scammell's process above-mentioned has been more successfully applied to the quantitative determination of cineol, and yields the most satisfactory results so far, although an error of several per cent. is scarcely avoidable.

There is some diversity of opinion on this matter, some chemists maintaining that a very close result is obtained, others that very large errors occur. In the author's opinion, in the hands of a careful worker, results accurate to within 3 per cent. can be obtained, so long as the cineol content is not below 30 per cent. If the amount of cineol is lower than this, the method is inapplicable, and the oil must previously be fractionated.

To a known weight of oil from 1 to 1½ times its weight of phosphoric acid of specific gravity 1·75 should be added, drop by drop, the oil being kept cold and continually stirred. The crystalline magma formed is pressed between filter paper, after as much as possible has drained off; and when the adherent terpenes and phosphoric acid have been removed as far as possible, the crystals are decomposed by hot water in a graduated tube. On cooling, the cineol is measured, and from its specific gravity (·930) the weight is easily calculated. The separated cineol should readily crystallise on cooling to − 3°, otherwise it must be regarded as impure and the process repeated. Oils rich in cineol yield a correspondingly high fraction distilling between 170° and 190°.

The great uncertainty regarding the term "eucalyptus oil" would be done away with by making the active ingredient, cineol or "eucalyptol" official in place of the oil. Its characters are well defined, and the article is easily made, and is a regular commercial product.

The chemistry and botany of this genus of the natural order *Myrtaceæ* require far more space than is available in the present work, to be dealt with thoroughly, consequently brief notes on the different species can only be given here. For

fuller information the reader is referred to the late Baron von Müller's classic monograph *Eucalyptographia*. The majority of the species are natives of Australia and Tasmania. A few occur in New Zealand and in certain of the islands of the Indian Archipelago, and a fair quantity of oil, especially from *Eucalyptus globulus*, is now obtained from Algiers, California and the south of France and Spain. The chief species whose oils have been examined are the following:—

Eucalyptus amygdalina.—This is the "narrow-leaved peppermint" or "brown" or "white" peppermint of Victoria, and is also found in South Australia, Tasmania, Victoria, and New South Wales. It is not found in Western Australia however. It is an abundant—indeed one of the most abundant, yielders of oil, as much as 4 per cent. being sometimes obtained from the leaves. It is one of the most colossal trees known, often reaching a height of 300 and sometimes 450 feet. At one time the oil was much esteemed, but as it contains very little cineol it has fallen into disfavour, and now commands a very low price. The oil, which is not particularly pleasant in odour, has a specific gravity of ·855 to ·890 and an optical rotation of $-25°$ to $-80°$. The main constituent of the oil is the terpene phellandrene, besides which the only known constituent is cineol, which occurs to the extent of from 5 per cent. in the low to about 25 per cent. in the high gravity specimens.

Eucalyptus Backhousia (*Backhousia citriodora*) is one of the sweet-scented plants generally known as a eucalypt, but which probably belongs to a different genus altogether. The leaves yield up to 4 per cent. of oil of aromatic odour, not at all resembling what is usually termed eucalyptus oil, of specific gravity ·895 to ·902. The constituent to which it owes its lemon-melissa-like odour is citral. Its other constituents are undetermined, but it probably contains a little phellandrene.

Eucalyptus Baileyana.—This is one of the numerous trees known locally as "stringy bark," and is confined chiefly to the north of New South Wales and the adjacent southern portion of Queensland. The leaves yield about 1 per cent. of oil, of a melissa-like odour, which, however, is partially covered by the cineol present. Its specific gravity is from ·890 to ·920 (specific gravities of ·940 to ·980 have been given, but these are hardly possible). It appears to contain up to 25 or 30 per cent. of cineol, some citral, and phellandrene.

Eucalyptus capitellata.—This tree is found in Victoria and Queensland. Its oil, which has not been examined, has an odour recalling that of peppermint. It has a specific gravity ·915, and contains about 35 to 40 per cent. of cineol and traces of a crystalline body, which has been named eudesmol.

Eucalyptus cneorifolia. — This eucalypt, one of the Mallees, is chiefly found in Kangaroo Island, South Australia. It is a comparatively small plant, seldom reaching more than 12 to 15 feet in height. It is known locally as the "narrow-leaved eucalyptus". The plant was originally looked upon as a variety of *Eucalyptus oleosa*, but it is now understood to be a separate species. The oil came into commerce some few years ago under the name of *oleosa*, but is quite different from the oil which was originally known under the same name. The oil is very rich in cineol, and has the high specific gravity ·915 to ·925, or even higher. Its optical activity is small, seldom exceeding 4° or 5° either way. It has a secondary odour recalling that of cumin. It contains from 50 to 70 per cent. of cineol and a small quantity of cumic aldehyde. This oil is much valued as a medicinal oil and conforms admirably to pharmacopœial requirements.

Eucalyptus corymbosa.—This is the New South Wales "bloodwood". It is found in this colony and in Queensland, chiefly near the sea coast. Its leaves yield about 4 pe

cent. of oil of specific gravity about ·880. It has an aromatic odour, according to Maiden, recalling that of lemon and roses. Sawyer states that it is rich in cineol, but this is incorrect. It contains a small quantity of cineol, and probably aldehydes of the geraniol series.

Eucalyptus crebra.—This is one of the many so-called "iron-barks" of Queensland. Its oil is bright yellow, and very rich in eucalyptol, closely resembling that from *Eucalyptus globulus.*

Eucalyptus dealbata.—This plant is confined to the drier portions of Queensland and New South Wales. Its oil, which is yielded to the extent of nearly 3 per cent. by the leaves, has a pleasant mellisa odour, and belongs to the class of sweet-scented eucalyptus oils. By many it is considered to possess a finer odour than any of the other eucalypts. The oil has a specific gravity of ·885 to ·900, and contains citronellal and either citronellol or geraniol. If the leaves be dried before distillation the oil is of a different character, and is said to have a specific gravity of over ·940.

Eucalyptus dextro-pinea.—This species has been described quite recently by Baker. It is a "stringy bark" of New South Wales, known as "messmate". Its botanical characters do not differ greatly from several other already described species, but its oil, which is yielded to the extent of about ·8 per cent., is characterised by containing a large amount of dextro-pinene. The oil is dextro-rotary, and of specific gravity ·873 to ·876. Small quantities of aldehydes were also detected (*see Eucalyptus laevo-pinea*).

Eucalyptus dumosa.—This plant is one of the Mallees (dwarf eucalypts forming the "scrub" of parts of Victoria, New South Wales and South Australia). The oil is of a good quality from a medicinal point of view, having a specific gravity of about ·900 to ·912, and containing from 30 to 50 per cent. of cineol. Its odour is strongly camphoraceous.

Eucalyptus eugenoïdes.—The leaves of this tree yield about ·7 per cent. of oil of agreeable odour. Its specific gravity is about ·905 to ·910, and its rotary power + 4° to + 6°. It contains from 25 to 35 per cent. of cineol and not any, or at most very little, phellandrene.

Eucalyptus globulus.—This tree, from which a typical eucalyptus oil is obtained, is the Tasmanian "blue gum". (Blue gum however is a name applied to a number of other eucalypts in New South Wales, Victoria and Western Australia.) This plant was discovered by Labillardière in Tasmania in 1792, and introduced into Europe in 1856 by Ramel. It is a native of Tasmania and Victoria, although found to a certain extent in other colonies. The fresh leaves yield from ·8 to 1·5 per cent. of oil of a light yellow colour, exceedingly rich in cineol. Eucalyptol, as it was then called, and as it is often termed to-day, was discovered by Cloez in this oil. The fact that this oil was regarded in Europe as the typical eucalypt yielding a medicinal oil, together with the occurrence of such numerous and closely similar species in Australia, account for the fact that eucalyptus leaves from various trees were indiscriminately mixed and distilled, the resulting product being marked oil of *Eucalyptus globulus*. Hence the difference observed by various chemists in the properties of this oil. The pure globulus oil, which is now a reliable commercial article, has a specific gravity of ·910 to ·930, and contains from 50 per cent. to 65 per cent. of cineol. It is dextro-rotary, from + 1° to + 10° (rarely up to + 15°). In addition to cineol it contains dextro-pinene, traces of ethyl and amyl alcohols and valeric, butyric and caproic aldehydes. This oil is the most valued of all the medicinal eucalyptus oils of commerce.

Eucalyptus goniocalyx.—This tree is known in Victoria as the "spotted gum" or "white gum," but in New South Wales it is usually spoken of as "blue gum". The oil is

bright yellow, of suffocating odour, of specific gravity ·915 to ·920, and contains some cineol.

Eucalyptus gracilis.—This tree inhabits the same districts as *Eucalyptus dumosa*, and is also found in Queensland. Its oil contains a fair proportion of cineol, and its cultivation has attracted some attention in Victoria.

Eucalyptus hæmostoma.—This is one of the many white gums of New South Wales and Queensland. The leaves yield about 2 per cent. of a nearly colourless oil, which is said by Dr. Bancroft to possess an odour intermediate between peppermint and geranium. Its specific gravity is ·880 to ·890. Cymene and cumic aldehyde have been detected in the oil, and possibly menthone also occurs. Schimmel & Co. consider it resembles cumin oil in odour.

Eucalyptus incrassata.—This plant is cultivated to a certain extent in Victoria, as yielding an oil with a fairly high cineol content. It has not, however, been closely examined.

Eucalyptus laevo-pinea.—This plant has recently been described as a new species by Baker. It is the silver top stringy bark of New South Wales. Very slight differences of a botanical nature exist between this tree and *Eucalyptus dextro-pinea* (*q.v.*), but the oil differs in that it consists chiefly of *laevo*-pinene, and contains only a very small quantity of cineol. The specific gravity of the oil is about ·873. Smith, who has examined these oils (*Eucalyptus dextro-pinea* and *laevo-pinea*), most unjustifiably suggests calling the pinenes he has separated from them by the names eucalyptene and eudesmene respectively. As a matter of fact the hydrocarbons he separated were merely ordinary pinene with some little impurity, so that the rotary powers were not exactly coincident with those known for this hydrocarbon, but to duplicate names in this free and easy fashion must only tend to restore that confusion which existed in the

terpene group before Wallach took up the task of correctly classifying them.

Eucalyptus leucoxylon is a "white gum" of Victoria and South Australia. It is also known as "boxwood" or "mountain ash". It is also found in Queensland and New South Wales. Its leaves yield rather over 1 per cent. of oil of specific gravity ·920 to ·925 with a fairly high cineol content.

Eucalyptus longicornis.—This plant is the morell tree of Western Australia, which is found on the sources of the Swan river, and onwards towards the east. Its leaves yield a high percentage of oil, but this has not yet been thoroughly examined.

Eucalyptus longifolia.—This tree, known as the "woolly-but" is found in New South Wales and in Gippsland, Victoria. The oil has a camphoraceous odour, but the sample of which an examination has been recorded had the high specific gravity ·940, and was possibly adulterated.

Eucalyptus loxophleba.—This tree is the York gum of Western Australia, so named on account of its frequent occurrence in the neighbourhood of York. It is found all over the eastern slopes of the Darling Range, and forms one of the valued timber trees of the colony. The oil has been examined by the author, who found it to contain only about 15 per cent. of cineol. It is dextro-rotary, about + 5° and has a specific gravity ·883. It contains phellandrene and another terpene, together with a considerable amount of aldehydes or ketones. It possesses a very irritating and offensive odour.

Eucalyptus macrorhyncha.—According to Baker and Smith, the leaves of this plant yield about ·3 per cent. of oil of a reddish-brown colour and of agreeable odour. Its specific gravity is ·927. The oil contains up to 53 per cent. of cineol, with traces of phellandrene and esters. The crys-

talline compound melting at 74° discovered by the above-named scientists, and termed by them eudesmol, is also present in considerable quantity.

Eucalyptus maculata var. citriodora.—This tree, the "citron-scented" eucalyptus, is found along the coast of Queensland and as far south as Port Jackson. It is a variety of the New South Wales "spotted gum" *Eucalyptus maculata* (which itself possesses very little odour). This variety yields the typical scented eucalyptus oil. The yield from the leaves is from 1 to 4 per cent. of an oil of melissa-like odour, of specific gravity ·870 to ·905, and slightly dextro-rotary to + 2°. It contains a very large quantity of citronellal, one specimen, according to Schimmel & Co., having been found to contain as much as 95 per cent. It also contains geraniol. This oil is of a most pleasant odour, and is admirably suited for soap perfumery, possessing a far more delicate odour than ordinary citronella oil, which it somewhat resembles in its general characteristics.

Eucalyptus microcorys.—This is the sallow wood of New South Wales or "turpentine tree" of Queensland. It yields from 1 to 2 per cent. of an oil of specific gravity ·895 to ·930. Cineol appears to be the only well-ascertained constituent, but according to some, the oil, when properly prepared, forms an excellent perfume.

Eucalyptus obliqua.—This tree is generally known as "strong bark" or "stringy bark" in Tasmania and Victoria. It is also found in New South Wales and South Australia. The leaves yield a fair quantity of oil of specific gravity ·895 to ·915 and optical rotation about − 7°. It contains both cineol and phellandrene in varying proportions.

Eucalyptus odorata. — Two trees are known by this name, the "white box" and the "peppermint" of the southern colonies of Australia. The leaves of the latter yield about 1·5 per cent. of an oil of specific gravity ·900 to

·925. It contains cineol, phellandrene and cumic aldehyde. It is said to be used to a certain extent in soap perfumery in Australia. The "white box" yields a very small amount of oil of specific gravity ·900 to ·922 containing much cineol.

Eucalyptus oleosa.—This tree forms one of the Mallee scrub group, which are all fairly rich in cineol. It is well-known in Victoria and South Australia and is also found in the interior extra-tropical parts of Western Australia. The leaves yield about 1·3 per cent. of an oil, of specific gravity ·905 to ·930 and optical activity − 5° to + 5°. It is very rich in cineol. According to Baron Müeller, it is the best known solvent for fossil resins, and "is unique for many technological applications". This oil is not identical with much of the so-called *Oleosa* oil of commerce, which is in reality obtained from *Eucalyptus cneorifolia.*

Eucalyptus piperita.—This is the New South Wales peppermint tree. Its leaves yield a large quantity of oil, but this is not well known in commerce, although it is manufactured in at least one district in New South Wales.

Eucalyptus populifolia.—This is the "bimbil box" of New South Wales, Queensland, and the northern territories of South Australia. The oil is bright red and contains cineol and cumic aldehyde. In odour it resembles cajuput oil.

Eucalyptus punctata.—Baker and Smith have described this as a variety of *Eucalyptus tereticornis,* known in New South Wales as grey gum. The yield of oil obtained was from ·63 to 1·19 per cent., its specific gravity ·9122 to ·9205. Of nine oils examined, two were *laevo*-rotary, from − 0° 55′ to − 2° 31′, and seven were *dextro*-rotary, from + 0° 32′ to + 4° 26′. The cineol content varied from 46·4 to 64·5 per cent., and no phellandrene was detected.

Eucalyptus Planchoniana.—This species is of limited occurrence, being found only in the northern parts of New South Wales and in South Queensland. The yield of oil,

which has a specific gravity ·915, is very low. It has been suggested as a soap perfume, its odour somewhat resembling citronella.

Eucalyptus resinifera.—This tree is known as the swamp gum. The oil yielded by the leaves is of a brilliant yellow colour, of specific gravity about ·900 and optical rotation − 15° to − 20°. It contains a fair quantity of cineol.

Eucalyptus rostrata.—This is a "red gum" common to all the colonies of the Australian mainland, being known as the "flooded gum of the interior". It is one of the most widely distributed eucalypts on the continent, and its timber has supplied more material for telegraphs, railways, bridges, etc., than perhaps any other tree in Australia. This tree, too, is the best known of all trees to the Australian explorers, for on it nearly all the old landmarks, camp locations and "signs" of the early explorers may be found cut. The tree has been introduced into Cochin China and Algeria, in both of which places it flourishes well. The oil has a somewhat powerful odour of valeric aldehyde, which body, together with much cineol, exists in the oil. This has a specific gravity ·915 to ·930 and an optical rotation of − 2° to + 13°.

Eucalyptus rudis.—This tree, according to Maiden, is known as a "blue gum" of Western Australia. The author has traversed the whole of the regions in which this tree is found, however, and finds that it is usually known as the "flooded gum". *Eucalyptus rostrata* just referred to is known as the "flooded gum of the interior," or commonly merely "flooded gum," and occurs on the littoral just south of the Murchison, whilst *Eucalyptus rudis* (as well as *Eucalyptus decipiens*), which occurs in the south-western portion of the colony, may be referred to as the "flooded gum of the south-west". The leaves yield a large quantity of oil, but its properties require examination.

Eucalyptus Risdonia.—The oil from the leaves of this

tree has a pleasant odour. Its specific gravity is ·910 to ·925, and its optical rotation – 2° to – 6°. Phellandrene and cineol, the latter in good proportion, have been found in the oil.

Eucalyptus salubris.—This is one of the Western Australian timber trees, its wood being largely used on the goldfields, where it is known as the gimlet gum. Its leaves yield, according to Müeller, 4 per cent. of oil, but its properties are not well known.

Eucalyptus Staigeriana. — This is the well-known "lemon-scented iron bark" of Queensland. The leaves when bruised have a strong verbena odour; indeed the oil closely resembles the latter in general properties. It is stated in the *Pharm. Journal* ([3], x., 212) that it can be distinguished from verbena oil by its lower specific gravity. This, however, is not so. The extraordinary statement also occurs that it has a specific gravity ·871, or, when freed from moisture, ·880, which means that by removing water with a higher specific gravity, the residual oil also increases in gravity! The characteristic odour is due to citral, which appears to be the chief constituent of the oil.

Eucalyptus Stuartiana.—This tree, which is found in Queensland, yields a yellow oil, with a strong odour of cymene. Very little, if any, cineol is present.

Eucalyptus terticornis.—This is one of the Queensland "red gums". It yields an oil somewhat resembling oil of zedoary in odour, and contains little or no cineol. It is of little value.

Eucalyptus tesselaris.—This tree yields an oil of a dark brown colour, and with an odour recalling benzoic acid. It contains no cineol.

Eucalyptus uncinata.—This tree is found in Western and South Australia, Victoria and South Australia. It is

one of the Mallees. The yield of oil is not very high, but the resulting oil contains a fair amount of cineol.

From the above brief remarks on the eucalyptus oils which are much known, it will be seen that they, broadly speaking, fall into three chief groups. The sweet-scented or perfume oils are few in number, and are typically represented by *Eucalyptus maculata var. citriodora* and *Eucalyptus Staigeriana*. The medicinal oils—those which contain a high percentage of cineol (eucalyptol)—are the most important group however; the requirements of the 1898 *British Pharmacopœia* narrow these down to comparatively few, which must have the characters therein described, and are therefore *British Pharmacopœia* oils. The typical oil—speaking from a popular point of view—of this class is that of *Eucalyptus globulus*, but it is a mistaken idea to think that there are not other oils of just as great value. Indeed, the oil of *Eucalyptus globulus* has its reputation from its label, as probably the majority of importations in the earlier days of this oil were mixtures, often without any globulus oil, in spite of their labels. The facts should be noted that not only are several other oils in accordance with the *British Pharmacopœia* requirements, but that many oils which do not quite agree with the limits prescribed by that standard are valuable oils of high cineol content. The third class embraces those oils which contain little or no cineol, and which are of very small value as compared with the other oils. The type of these oils is, perhaps, that of *Eucalyptus amygdalina*. The recognised value of cineol, and the ease with which it can be prepared, result in the manufacture of pure cineol, which is known commercially as eucalyptol. In the author's opinion, eucalyptus oil as an *official* drug might well be replaced by eucalyptol, whose properties are very definite, *viz.*, specific gravity ·930; optically inactive; solidifying at low temperatures and re-melting at $-1°$; boiling at

176°. There is only one danger in this, *viz.*, that if eucalyptol were made official the oil would naturally be removed from the *Pharmacopœia*. The public, however, know the oil so well that they would continue to demand it, and any of the almost valueless oils, such as *Eucalyptus amygdalina*, could then be sold with impunity.

Cajuput Oil.—This oil is distilled from the leaves of several species of *Melaleuca*, myrtaceous shrubs growing abundantly in the Indian archipelago, the Malay peninsula, and other places. Most of the oil of commerce is yielded by *Melaleuca minor* or by *Melaleuca leucadendron*. The oils from these two trees can scarcely be distinguished. The *British Pharmacopœia* gives *Melaleuca leucadendron* (*Melaleuca cajuputi*). A great portion of the oil is distilled on the islands of Bouru and Banda, whence it is brought to Macassar and the neighbourhood for shipment. The bulk of the oil is exported in wine bottles, although shipment in drums, to save the excessive freight, has been resorted to. The oil has a powerful camphoraceous odour, due largely to its high cineol content. It is usually of a green colour, generally due to contamination with copper, but can be obtained white by re-distillation. The specific gravity varies from ·920 to ·930, although the *Austrian*, *Italian* and *Japanese Pharmacopœias* allow a rather lower limit. The present edition of the *British Pharmacopœia* gives ·922 to ·930. The oil is almost optically inactive, usually varying from 0° to − 2°. Normal oil contains up to 65 per cent. of cineol. In addition to this body, to which the oil owes its value, terpineol and terpinyl acetate have been found, and, according to Voiry (*Jour. Pharm. Chim.*, 1888, p. 149), butyric, valeric and benzoic aldehydes and probably laevo-pinene. The low specific gravity of many commercial samples is accounted for by adulteration with turpentine, or by abstraction of the cineol. The oil is not used to any

extent internally, but is employed externally as a stimulant and anti-spasmodic. Eucalyptus oil with a high cineol content is well able to replace it for most purposes. Genuine cajuput oil should contain at least 55 per cent. of cineol, as estimated by the phosphoric acid process.

The oil from *Melaleuca viridifolia*, a plant growing abundantly in New Caledonia, has been examined by Bertrand. The leaves when fresh yield about 2·5 per cent. of a pale yellow oil, generally known as "essence de Niaouli," with an odour resembling that of cajuput. The sample examined (*Comptes Rendus*, cxvi., p. 1070) had a specific gravity ·922 and a rotary power + 0° 42′. Traces of valeric and benzoic aldehydes are present in this oil, the greater part of which consists of cineol and a terpene, probably pinene. A little terpineol is also probably present, and possibly traces of limonene. Maiden has described a number of species of *Melaleuca* indigenous to Australia. The physical properties of the oils from them are as follows :—

	Specific Gravity.	Boiling Point.	Rotation.
Melaleuca decussata .	·938	183°-209°	—
Melaleuca ericifolia .	·899-·902	149°-184°	+ 26°
Melaleuca linarifolia .	·903	175°-187°	+ 11°
Melaleuca Wilsonii .	·925	—	—
Melaleuca uncinata .	·925	175°-180°	+ 1° 40′
Melaleuca leucadendron, *var. lancifolia* .	·955	—	− 3° 38′
Melaleuca acuminata .	·892	—	− 15° 20′

Myrtle Oil. — This oil is distilled from the leaves of *Myrtus communis*, probably a native of the south of Europe, although possibly it was introduced here from western Asia. So long ago as 1867 Gladstone examined this oil, but his results are of little value to-day. The specific gravity of the oil varies from ·895 to ·915, or ·920 at times. The rotation is to the right, from + 10° to + 25°. Jahns has shown that this oil contains dextro-pinene, cineol and a

camphor of the formula $C_{10}H_{16}O$. Probably dipentene also is present. Under the name "myrtol," the fraction of the oil boiling between 160° and 170° has been introduced into commerce. It is not a definite compound, and probably possesses little value. The oil is sometimes used medicinally, but probably a little cineol would be more useful than myrtle-leaf oil in any case where it might be required.

Cheken-leaf Oil is the product of distillation of the leaves of *Myrtus cheken*, indigenous to Chili. The yield is about 1 per cent. of a pale yellowish-green oil, much resembling ordinary myrtle oil. According to Weiss, its specific gravity is about ·880, and its optical rotation about + 20°; it consists of pinene (75 per cent.), cineol (15 per cent.), and substances not further examined.

N. O. Rosaceæ.

Oil of Roses.—Of the numerous varieties of the rose, only a very few are used for the preparation of oil or "otto" (attar) of roses. Climate and soil have so marked an influence on this plant, that a few varieties are found to grow to perfection in special localities, and these alone are cultivated for the purpose of obtaining the oil. Not only does the sweet and characteristic odour of rose vary much amongst the different varieties, but many of these are practically odourless, and some even objectionable in this respect.

The "*rose garden of the world*," as it has been fittingly called, is situated in the Balkans, and from Bulgaria and Roumania nearly the whole of the otto of rose of commerce is obtained. The most important centre of the industry is Kezanlik. The area under cultivation is included between the 24th and 26th degrees of longitude east and the 42nd and 43rd degrees of latitude north. The geological formation is chiefly syenite, the decomposition of which has produced a very fertile soil. The roses flourish best in sandy sun-

exposed slopes, with a south or south-eastern aspect. The most important districts are (1) the department of Stara-Zagora, including the cantons of Kezanlik, Nova-Zagora and Stara-Zagora; (2) the department of Pazardjik, chiefly the canton of Pechtera; (3) the department of Philippopolis, including the cantons of Karlovo, Tchirpan, Novo-Selo and Brezovo. The flowers are gathered before they commence to open, in the early morning just before sunrise, and the picking continues till ten or eleven o'clock, or on cloudy days during the whole day, as it is important that the roses

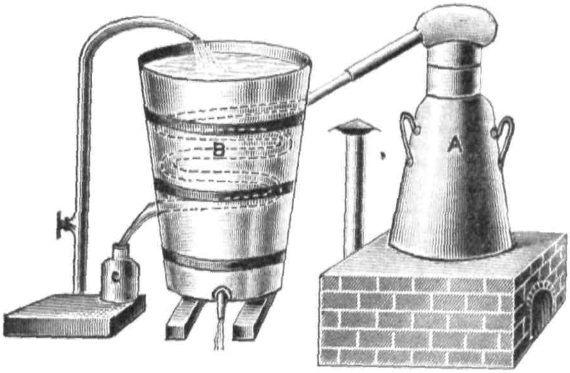


FIG. 20.—A, copper alembic; B, condenser; C, receiver.

should not be picked when the sun's heat is on them. A garden of an acre when well planted will yield about 100 pounds of flowers every day for three weeks. The roses are carried to the distilleries, which are very numerous, and distilled as quickly as possible. However, if the flowers come in too quickly they are sometimes left for twenty-four hours before being distilled, the resulting oil being thereby impaired in value. The distilleries are primitive buildings, sometimes little better than wooden sheds. On one side the stills are kept in rows. These are copper alembics about 3 to 5 feet in height, resting on a furnace built of bricks. The

average content of each still is about 20 gallons, the charge usually being 10 kilos of flowers and 75 litres of water.

The condenser is a straight or worm tube passing through a vat of water, into which cold water continually runs. A brisk fire is kept up for an hour to an hour and a half, and when 10 litres of liquid are obtained the fire is drawn. At times 15 litres are distilled over, but the result is an otto containing a larger amount of stearoptene. The still is then opened and the spent petals, or rather flowers, for the green plants are seldom separated, are thrown away, and the residual hot water is returned to the still with cold water to make up the 75 litres, and a fresh charge of flowers. This operation is repeated until, as a rule, 40 litres of rose water have been collected. These 40 litres are now distilled, and the first 5 litres are collected in a long-necked flask. The residual 35 litres are used for distilling fresh flowers. The 5 litres distilling over are cloudy, and the oil drops gradually rise and collect in the neck of the flask. When it has all risen, it is removed by a small tin funnel with a tiny orifice for the water to drop out of. The yield is variable, a warm humid spring with intervals of strong sunshine being more favourable than an uninterrupted hot dry season. The average yield in Bulgaria is about 1 kilo of otto from 3,000 kilos of rose leaves. The rose cultivated in this district is *Rosa damascena*, a red rose, but the hedges of the plantations are often made up of *Rosa alba*. The latter are not often distilled, as the yield is very poor, but as the resulting oil contains more stearoptene than the *Rosa damascena*, the farmers occasionally distil the white rose in order to be able to adulterate the otto with more geranium oil, without reducing the melting point below a certain minimum; for the melting point is taken in the district as the criterion of value of the oil. The difficulties in acquiring exact knowledge on many points connected with

oil of roses has been largely enhanced by the fact that adulteration is almost universal. The usual adulterant is the so-called Turkish geranium oil (Indian geranium oil from *Andropogon schoenanthus*), and in spite of stringent regulations, and seizure of smuggled geranium oil, the practice still goes on to an enormous extent. It is surprising that an industry of so much importance should have been allowed to go on for so many years fettered by two such great evils; firstly, the almost universal adulteration practised, secondly, the defective methods of preparation, resulting in the spoiling of the fine odour of much of the otto. Although climate and soil have so great an influence on the yield and quality of the oil, there can be no doubt that there are localities where rose cultivation and distillation could be carried on in a scientific as well as an honest way.

Formerly the Turkish dealers were responsible for the greater part of the adulteration, but now the small growers come in for their share of the illicit profits, and not only do they add the adulterant to the distillate, but frequently sprinkle the leaves with geranium oil before distillation, believing that they so obtain a better "blend".

The value of a pure oil depends on the quality of the flowers used and on the care taken in distillation. It also depends on the amount of solid stearoptene present, for this portion of the oil is quite inodorous.

The value of otto in the locality of its distillation is gauged almost entirely by its melting point. Consequently spermaceti or even paraffin wax has been added to counteract the reducing influence of the liquid geranium oil. Recently, too, guaiacum wood oil (so-called), an oil of fine odour which solidifies with a fine crystalline structure at ordinary temperatures, and consists of bodies much resembling those in oil of roses, has been used as an adulterant.

In this connection it may be mentioned that no standard

for the quantity of stearoptene present in natural rose oil can be fixed, as climatic conditions appear to influence the ratio of the solid to the liquid portion very greatly. From 10 to 20 per cent. occurs in Bulgarian oil, whereas that obtained in the south of France, in England and in Germany, has been stated to contain from 25 to 65 per cent. of stearoptene. In the case of so high a content as the latter figure it is certain that the oil was not prepared in the normal way, probably being the result of the distillation of rose water.

Roses are cultivated to a very large extent in the south of France in the neighbourhood of Grasse, Cannes and Nice. Here, however, the variety most cultivated is *Rosa centifolia*. The flowers are used chiefly for the preparation of rose water and rose pomade, very little oil being manufactured, and practically the whole of this is used in France itself, seldom appearing to any great extent on the English market. Here the flowers are also picked in the early morning, as many as 150 tons of flowers being gathered on a single day in the province of the Alpes Maritimes. The petals are usually entirely separated from the green parts in France. The otto produced here is of very exquisite odour.

In Germany, Messrs. Schimmel & Co. have laid out extensive plantations near Klein-Miltitz, and although the natural resources of climate and soil are not so favourable here as in Bulgaria or southern France, the scientific and careful way in which the oil is obtained, to a certain extent counterbalances this, and a fairly fine otto is obtained. In Algeria, a small amount of otto is produced, but the yield is less than in Bulgaria. In Persia and Cashmere, however, it is said that nearly one pound of otto is obtained from 1500 to 2000 pounds of petals.

Oil of roses is not an easy oil to form an opinion upon with any degree of certainty. Gross adulterations can easily

be detected, but judicious admixtures of rose and geranium oils are less easy to deal with. The *British Pharmacopœia* requires that the specific gravity at 30° should be between ·856 and ·860, and the congealing point from 19·4° to 22·2°. The figures ·855 and ·865 at 30° may be taken as including most good commercial otto, although there is little doubt that these figures are not representative of all oils produced under all conditions. The oil is nearly inactive optically, and + 1° to − 4° may be regarded as safe limits. The limits for the congealing point for the pure Bulgarian oil may be taken as from 17° to 23°, usually about 20°, but oils from other districts frequently have a higher congealing point than this. To exemplify the difference in the physical properties of certain oils produced in other districts, the following may be quoted. A Persian oil, believed by Schimmel & Co. to be pure, gave the following figures :—

Specific gravity at 25°	= ·8326
Optical rotation .	. = − 9° 7′
Congealing point	. 21·5°

Dupont has given the optical rotation for French oil up to − 8°, and this is amply confirmed by other observers.

The addition of geranium oil (Indian) may cause a rise in the specific gravity sufficient to bring that of the oil outside the limits given above, but in moderate quantity may avoid detection in this way. The optical rotation will scarcely be affected, but the congealing point will be lowered, and if the original otto contained only a moderate quantity of stearoptene, this figure will be reduced below the minimum allowable for pure oils. An examination of the stearoptene thus becomes necessary. By addition of alcohol and freezing, the stearoptene can be almost entirely separated on a filter pump and washed with alcohol and finally dried. It should then melt between 32° and 37°, usually at 33° to 34°. Spermaceti, and most samples of paraffin wax, will cause this to be rather

higher, as will also "guaiacum wood" oil if present in more than very small quantities.

Spermaceti or stearin will be easily detected, whilst paraffin wax or the solid constituent of guaiacum wood oil (which is of an alcoholic nature) are not so easy of detection. As the stearoptene of pure rose oil consists of hydrocarbons, no fatty acids will be obtained by saponification, whereas spermaceti and stearin will yield on saponification and decomposition of the resulting salts with hydrochloric acid, palmitic and stearic acids respectively, which may be identified by their melting points (palmitic acid from 55° to 62°, and stearic acid from 62° to 68°). Paraffin will be indicated by the more granular structure of its crystals than that of the normal stearoptene, whilst the solid portion of guaiacum wood oil consists chiefly of a solid alcohol and will yield an acetyl figure, which is not the case with the normal stearoptene.

The percentage of free alcohols in the oil usually varies from 70 to 75 per cent., estimated as geraniol, by acetylation Geranium oil gives from 75 to 95 per cent., so that no definite information is yielded in this way. Dietze (*Sudd. Apotheke Zeitung*, xxxvii, [89], p. 835) strongly recommends the acid and ester values to be determined by titration, and saponification with semi-normal alcoholic potash. This gives the following figures (in percentages of potash):—

	Acid.	*Ester.*	*Saponification.*
German rose oil . .	·21	·65	·86
Bulgarian . . .	·12	·80	·92
,, ...	·14	·75	·89
French geranium . .	·68	4·79	5·47
,, ,, . .	·50	5·41	5·91
African ,, . .	·75	4·56	5·31
Spanish ,, . .	·98	7·19	8·17
Indian ,, . .	·15	3·10	3·25

Whilst there is no doubt that the ester value of mo geranium oils is higher than that of rose oil, the above figur are not comprehensive enough, and the indications obtain

would be of very little value in the case of admixtures of considerable quantities of geranium oil.

Of the chemistry of oil of roses, although fairly well understood now, much controversial matter has been written. Eckart ("Inaugural Dissertation," Breslau, 1891) states that a small quantity of ethyl alcohol exists in the oil. If this is so, which Poleck denies, it is in all probability the result of fermentation taking place in the leaves, by keeping them too long before distillation. Markovnikoff and Reformatsky originally stated that the liquid portion of rose oil consisted chiefly of an alcohol of the formula $C_{10}H_{20}O$, which they termed roseol. Poleck and Eckart claimed that this alcohol had the formula $C_{10}H_{18}O$, and was identical with geraniol. They however proposed the name rhodinol (which was applied to an alcohol $C_{10}H_{20}O$ from geranium oil by Barbier and Bouveault) for it. Bertram and Gildemeister then showed that the alcohols from rose oil were in reality a mixture of two bodies, of which they agreed that geraniol $C_{10}H_{18}O$ was the chief constituent. Tiemann and Schmidt explained these differences, proving that the alcohols consisted of about 75 per cent. of geraniol $C_{10}H_{18}O$ and 25 per cent. of an alcohol $C_{10}H_{20}O$, which was identical with that obtained by reducing citronellic aldehyde. Hence they naturally insisted on the name citronellol. Much confusion has unnecessarily been caused by various chemists giving names to alcohols they had isolated from different oils in an impure state, and refusing to alter these names after it had been conclusively proved that they were, when pure, identical with already known bodies. Lemonol, rhodinol, réuniol and roseol are all either geraniol or citronellol, or mixtures of them. Traces of esters of these two alcohols, and of free acids resulting from their decomposition also occur. The stearoptene was regarded by Markovnikoff as consisting of a single paraffin hydrocarbon of the formula $C_{16}H_{34}$, melting at 37°, but Schimmel & Co.

have separated two hydrocarbons melting at 22° and 41° respectively, from the stearoptene. This has been confirmed by Dupont and Guerlain. These chemists suggest that the ester, which appears to be found in larger quantity in French oils than in any other, is an important odoriferous constituent, and is destroyed by repeated distillation with water. They separated the liquid portion of the oil and found it had an optical rotation of − 10° 30′, which decreased to − 7° 55′ after hydrolysis. Charabot and Chiris invariably find rose water acid, which tends to confirm this hypothesis.

It must be admitted that the sense of smell is one of the most useful criteria of the purity of this oil, and, on account of the high price and wholesale adulteration, it is imperative that the oil should be purchased through a reliable source. Its sole employment is for the purposes of perfumery; its employment in pharmacy being merely to scent various preparations.

Oil of Bitter Almonds.—The true bitter almond oil is obtained by distilling the seeds (almonds) of *Amygdalus communis var. amara* with water after the fixed oil has been extracted by expression. The kernels of the apricot and peach yield essential oils practically identical with that from the almond, and the greater part of the bitter almond oil of commerce, especially the foreign oil, is obtained from the former (*Prunus armeniaca*). The following remarks may be taken as generally applicable to all three oils:—

Bitter almond oil does not exist as such ready formed in the seeds (almonds, kernels). It results from the action of water on the glucoside amygdalin, under the influence of the natural ferment emulsin, present in the seeds. The reaction taking place is expressed by the following equation:—[1]

[1] Brannt (*Animal and Vegetable Fats and Oils*) gives the following extraordinary and erroneous reaction:—

$$2C_{20}H_{27}NO_{11} = 4C_7H_6O + 2HCN + C_6H_{12}O_6 + 4CH_2O_2 + 4H_2O.$$

$$\underset{\text{Amygdalin.}}{C_{20}H_{27}NO_{11}} + 2H_2O = \underset{\text{Benzaldehyde.}}{C_7H_6O} + \underset{\text{Dextrose.}}{2C_6H_{12}O_6} + HCN.$$

Amygdalin, taking up two molecules of water, yields benzaldehyde, dextrose and hydrocyanic acid. Amygdalin is a crystalline body, without any smell of the bitter almond and does not yield the oil except under the influence of a hydrolytic agent, such as the natural ferment emulsin, or by boiling with dilute acids. The action of the ferment is destroyed by heat or by warm alcohol. Hence if dried and powdered bitter almonds are shaken with boiling water and distilled, no oil is obtained. After the fixed oil has been expressed the press-cakes are ground up and soaked for about twenty-four hours in twice their weight of water, to which a quantity of salt is usually added. The whole is then subjected to distillation. Some trouble, however, is experienced during the process, as the large quantity of albuminoids present causes excessive frothing. To remedy this, the press-cakes are coarsely powdered and at once immersed in boiling water to coagulate the albuminoids and dissolve the amygdalin. The emulsin is, of course, rendered inactive, so that on cooling, a quantity of emulsion of the fresh cake in cold water is added to the previously treated mass. This is allowed to stand, until the emulsin will have converted the whole of the amygdalin into essential oil. The mixture is now distilled. As hydrocyanic acid is a very deadly substance, it is necessary to use great care that none of the vapour is allowed to escape into the air. The distillation is effected by direct steam in most cases. The oil of almonds so obtained contains a considerable amount of hydrocyanic acid, the remainder being almost pure benzaldehyde, $C_6H_5 . COH$. The absolutely natural oil is a regular commercial article, but much is deprived of its hydrocyanic acid before being sold, and is then listed at a correspondingly high price as "Oil of Almonds (S.A.P.)"

(*i.e.*, *Sine Acid. Prussic.*). The following methods are used to deprive the oil of this poisonous constituent:—

The oil is mixed with its own volume of water and the mixture left on a water bath with red oxide of mercury, slaked lime and ferrous chloride, out of contact with the air. After all the prussic acid has been decomposed, the oil is rectified and contains no trace of prussic acid. This process was suggested by Redwood. Liebig used oxide of mercury only. Mackay prefers agitating at intervals for forty-eight hours with a mixture of lime and liquor potassæ. To detect any traces of prussic acid left in the oil, a little of it is dissolved in alcohol, and a little solution of potash and a little solution of ferrous sulphate are added. On the addition of a dilute acid, Prussian blue appears if any hydrocyanic acid is present. Benzaldehyde is very readily oxidised by the oxygen of the atmosphere to benzoic acid, so that the oil almost invariably contains traces of this body, and if kept in bottles that are not quite full the oxidation becomes more rapid, and crystals of benzoic acid are deposited. This is more especially the case when the oil has been freed from prussic acid. According to Schimmel & Co., 10 per cent. of alcohol added to the oil retards this oxidation.

Benzaldehyde is very easy to manufacture on a large scale by numerous processes, consequently artificial oil of almonds (not to be confounded with the coarse imitation oil, nitrobenzene or mirbane oil) is now a regular commercial article, and may be obtained in various grades of purity. Although very useful for the cheaper grades of perfumery, this artificial oil does not possess the delicate odour of the natural body. To get the best results the artificial oil should be obtained free from chlorine, which is usually present in the cheap commercial article. The usual methods of preparing benzaldehyde are by heating two parts of benzyl chloride with three parts of lead or copper nitrate and ten parts of water in

a current of carbonic anhydride for some hours under a reflux condenser. Half the liquid is then distilled off and the oil separated. Or benzal chloride $C_6 . H_5 . CHCl_2$ is heated in an iron vessel with lime or soda, under pressure. Pure benzaldehyde is a colourless mobile liquid, of specific gravity 1·050, boiling at 179°. It is more soluble in water than most essential oils.

Natural almond oil is, in the crude state, a yellowish liquid, but is white when rectified, of specific gravity 1·045 to 1·070, but usually from 1·045 to 1·055. It is optically inactive. It is often adulterated with artificial benzaldehyde, and if the purest variety be used it is impossible, within certain limits, to detect it, except, possibly, by the nose. If the cheaper variety has been used, chlorine compounds will be present and may be detected as follows. A piece of filter paper is saturated with the oil and placed on a small porcelain dish standing in a larger one. A large beaker whose sides are moistened with distilled water is stood over the smaller dish, the paper having been set alight. The gases generated by the combustion are, to a certain extent, absorbed by the water on the sides of the beaker, which is rinsed out with a little more distilled water. The liquid is filtered, and one drop of nitric acid and a few drops of solution of silver nitrate are added to the filtrate; the formation of insoluble silver chloride is strong evidence that artificial benzaldehyde is present.

Another adulterant, of a much grosser character, is oil of mirbane. This is the cheap almond oil substitute so largely used for perfuming cheap toilet soaps. Chemically it is nitrobenzene $C_6H_5NO_2$, more or less mixed with impurities, of which the most common is nitrotoluene, which sometimes itself forms the greater part of cheap nitrobenzene. Indeed, nitrotoluene in any great quantity may be regarded as an adulterant of nitrobenzene. The latter, when pure, is a

yellowish liquid of specific gravity at 0° of 1·200, boiling at about ·206°, and solidifying at + 2° to + 3°. It has a coarse almond-like odour, and is poisonous when taken internally, and irritating to the skin when used externally. The cheapness of artificial benzaldehyde should discourage its use in even the very cheap toilet soaps. Nitrotoluene $C_6H_4(CH_3)NO_2$ exists in three isomeric modifications, and nitroxylene $(C_6H_3)(CH_3)_2NO_2$ in more still. It is these bodies which are found to a considerable extent in the cheaper qualities of nitrobenzene. Consequently it is important that commercial samples should have physical characters in approximate agreement with those above quoted.

To detect the presence of this objectionable substituent in oil of almonds a little of the oil is warmed with iron filings and acetic acid. The nitrobenzene is reduced to aniline $C_6H_5NH_2$, which is distilled off and collected. To the distillate a few drops of solution of ordinary chloride of lime is added. If aniline be present the liquid yields the characteristic violet colour. Pure benzaldehyde combines with sodium bisulphite to form a crystalline compound without the characteristic almond odour. Samples adulterated with nitrobenzene, when shaken with excess of bisulphite of sodium solution, so that the benzaldehyde is entirely combined, then have the characteristic coarse nitrobenzene odour.

This oil is used in confectionery, perfumery, and, to a small extent, in medicine. The following are the approximate values of the various oils mentioned in the above paragraph, in ordinary wholesale quantities :—

Pure natural oil from almonds . .	25s. per lb.
,, ,, ,, ,, apricots . .	18s. to 20s. per lb.
Pure benzaldehyde, free from chlorine .	7s. 6d. per lb.
Commercial benzaldehyde . . .	2s. 6d. to 3s. per lb.
Mirbane oil	6d. to 8d. per lb.

The natural oils, freed from prussic acid, are worth from 2s. to 4s. per lb. more.

Cherry Laurel Oil is distilled from the leaves of *Prunus laurocerasus*, an evergreen shrub, a native of south-eastern Europe and Asia Minor. Most of the oil is distilled in the south of Switzerland and in Italy. It is obtained also in England and Germany, together with the official cherry laurel water, by distilling the leaves in the ordinary way. The oil is optically inactive, and has a specific gravity 1·050 to 1·065. It contains benzaldehyde, prussic acid, and possibly traces of benzyl alcohol, and, indeed, differs very little from oil of bitter almonds.

Wild Cherry Bark Oil.—The bark of *Prunus virginiana* yields about ·2 per cent. of essential oil of specific gravity about 1·050, and optically inactive. It contains benzaldehyde and prussic acid, and closely resembles oil of bitter almonds.

Oil of Meadowsweet.—This oil is obtained by distilling the herb *Spiræa Ulmaria.* It contains salicylic aldehyde $C_6H_4(OH)(COH)$, a terpene, and a camphor-like substance. The oil is artificially prepared by distilling salicin, the glucoside of this plant, with chromic acid. If the distillation is carried too far a little furfurol also comes over, which causes the oil to become very dark on keeping. The oil is but little used.

N. O. RUTACEÆ.

Lemon Oil.—This oil, one of the most important of all the essential oils from the commercial point of view, is obtained by various processes from the fresh peel of the ordinary lemon, *Citrus limonum.* The tree is a native of India, and was introduced into southern Europe, probably first into Spain, and thence to the south of France and Italy. There are numerous varieties and hybrids, but the ordinary lemon

forming the fruit of commerce is the Genoese lemon. This is cultivated on the Mediterranean littoral, especially between Nice and Genoa, in Calabria, Sicily, Spain and Portugal, and on nearly the whole coast of Liguria. The oil is obtained between the months of November and March, or April, and the processes used are the following (which have been already described in detail, *see* page 63 *et seq.*). (1) The Spugna or sponge process, by which the oil is removed from the burst oil cells of the peel by a sponge. (2) The Ecuelle method, by which the lemons are rolled about in vessels covered with spikes and the oil collected in a receptacle in the handle of the vessel. (3) Machine processes, such as the thermo-extractor described on page 66. (4) Simple distillation. This method gives a very inferior oil, and is often applied to the peels from which all the oil obtainable by other processes has been obtained. (5) Expression in bags in ordinary presses.

The sponge method is the typical process in use in the chief lemon oil districts—Sicily and Calabria; the ecuelle method being employed chiefly in the south of France and north of Italy, and to a certain extent, of course, in the south.

The oil, though fairly constant in its characters when pure, varies according to the period of the harvest, the weather and the locality. For example, the oil obtained during the first two months of the season—November and December — is usually of the finest character, and also possibly as a coincidence only, usually possesses the highest optical rotation.

The greater part of the oil of commerce is produced in the district of Messina, on the north-east of the island of Sicily and the adjacent districts along the coast to the west; a considerable amount is produced in the Palermo province and all along the east coast of the island; and a lar

amount also in Calabria, which is chiefly exported from Reggio. An approximate idea of the relative production of these districts is seen from the export returns during 1896, which were as follows :—

From Messina	. . . .	462,611 kilos.
,, Reggio	. . . .	50,856 ,,
,, Palermo	. . . .	32,462 ,,
,, Catania	. . . .	7,585 ,,

Apart from the alteration in rotary power suggested above as coinciding with the time of the crop, although possibly having no direct relation to the quality of the oil, Messrs. Schimmel & Co. assert that the oil obtained from round about Barcelona (near the northern coast) and from the plains of Syracuse (on the south-eastern coast) possess the highest average rotations of all the oils, this figure varying from + 64° to + 67°. They give the following figures for the various districts :—

From + 59° to + 61° . .	Messina and neighbourhood, Nizza di Sicilia.
,, + 61° to + 63° . .	Acireale, S. Teresa di Riva, Scaletta, S. Lucia, Patti, S. Agata, S. Stefano.
,, + 63° to + 64° . .	Catania, Giarre, Giardini, Acireale, Lentini.
,, + 64° to + 67° . .	Barcelona, Syracusa.

The Palermo oils are given at + 59° to + 61°, and the Calabrian oils at + 59° to + 62° 30′. In the author's experience these limits are of very small value and cannot be taken as in the least degree conclusive. Cool rainy weather appears to have some effect on the optical rotation, but all one can say conclusively is that the average rotation observed during one season's crop is sometimes 2° or 3° higher or lower than that of the preceding year. The Palermo oil and the Messina oil differ somewhat in their odour, etc., so that a trained nose can discriminate between them. This difference has been, to a certain extent at all events, explained by Umney and Swinton (*vide infra*).

The well-defined constituents of lemon oil are the terpenes

dextro- and *laevo*-limonene, which form the greater portion of the oil. It is doubtful whether any other hydrocarbons are present, except traces of phellandrene. Cymene and pseudo-cymene have been stated to occur, and also pinene, but the latest researches tend to show that none of these bodies are present in the pure oil. Indeed, Schimmel & Co. fractionated fifty kilogrammes and were unable to find even traces of pinene. Of the oxygenated constituents, which occur to the extent of under 10 per cent., the aldehyde citral is the most important, and is the chief odour-bearer of the oil. It occurs to the extent of 5 to 7 per cent. in pure oils. Traces of the aldehyde citronellal are also present. An alcohol $C_{10}H_{17}OH$ and its acetate, were, some years ago, stated to have been found, and this statement has recently been confirmed by Umney and Swinton, who identified about 1 per cent. of geranyl acetate in the oil. In Messina oil, only geranyl acetate was found, whereas in Palermo oil a little linalyl acetate was also identified. This slight difference may account for the difference in odour between the two oils (*Pharm. Journ.*, 1898, series iv., p. 1475).

Possibly a sesquiterpene is present in very small quantity. Two crystalline substances have also been found, one by Tilden and Beck, possessing the formula $C_{14}H_{14}O_6$, and melting at 115° to 116°, and the other by Crismer, $C_{10}H_{10}O_4$, melting at 144°. Probably other bodies exist in the small quantity of stearoptene found in the oil.

Adulteration, which was until recently almost universal, is still very common. Turpentine was the regular adulterant, with, at times, the poorer quality distilled oil of lemons. But adulteration with turpentine is now so easily detected that the sophistication is frequently carried out in a more scientific manner. Mixtures with the proper specific gravity and optical rotation can easily be made up from turpentine and orange oil—the poorer qualities of the latter of course being

used—and such mixtures are often used to adulterate the oil with. But the most formidable adulterant from the analyst's point of view is one that has only come into vogue during the last few years, *viz.*, the terpenes obtained in manufacturing the "terpeneless" or concentrated oils of lemon and oil of orange, the latter being sometimes added to turpentine to bring up the optical rotation.

The terpenes are sometimes used alone, sometimes together with a little citral obtained from lemon-grass oil. Before discussing the analysis of lemon oil, a few words on the citral content will not be out of place. It is a common custom to export oil of lemons with a guaranteed citral content, and to sell it upon that basis. In judging of the value of such a basis for the market value of the oil, the following points should be carefully noted. Firstly, that there is no absolute method of estimating the amount of citral yet published, and the results are only approximate and worthy of very little attention unless the method of analysis be given; secondly, that it is a common practice to add a little citral, obtained from lemon-grass oil, either alone or together with lemon-terpenes, to the oil; so that if an accurate method were known the interpretation of the result is impossible and meaningless.

Lemon oil is apt to deteriorate on keeping. It will often become cloudy and paler in colour and develop an unpleasant odour. The traces of water dissolved in the oil, and afterwards separating out, are responsible for the turbidity, but the general deterioration is undoubtedly due to chemical change in which the terpene plays the chief part. To keep the oil most perfectly it should be stored in bottles quite full, to avoid contact with air, and in a cool dark place. Absolute alcohol is also added to the oil for the purpose of keeping it.

The specific gravity of a pure lemon oil should vary between ·857 and ·862. These limits are rarely exceeded,

and when they are, only fractionally. The optical rotation taken at 20° should not be less than + 59°, and is usually between this figure and + 64°, although undoubtedly pure samples are occasionally found with a rotation up to about + 66°. Increase in temperature causes a slight diminution in rotary power, but this does not amount to more than about − 8′ or − 9′ per degree rise in the temperature of the oil. Pure lemon oil commences to boil at 170° to 172°, and from 20 to 30 per cent. will be obtained from 172° to 174°. However, the percentage of the fractions at temperatures near to one another are so dependent on the exact form of the fractionator, that the results are not constant enough to be of much value, unless any oil distils below 170°. The estimation of the citral present has long been regarded as the most important point to be considered in the analysis of the oil, and much regret has been expressed that no accurate quantitative method is known. Shaking the oil with bisulphite of sodium solution is probably the process used by those analysts who return a citral content in lemon oil, but apart from the fact that the process is not accurate, the occurrence of citral in lemon-grass oil to the extent of 80 per cent., makes it an easy matter to add a little citral to the oil, a practice which is very common in Sicily. A very important method of judging of the purity of oil of lemon consists in an examination of the optical rotation of the fractions into which the oil can be separated by distillation. Soldaini and Bertè proposed the examination of the first 2C per cent. obtained by careful distillation. They stated that this fraction always possessed a higher, and the residue a lower, rotation than that of the original oil. They have since, however, modified this view. Schimmel & Co. state that the first 10 per cent. distilled always possesses a lowe rotation than that of the original oil, a conclusion with whicl the author's experience agrees. Mancuso Lima proposed t

shake the oil with bisulphite of sodium solution, and distil the terpenes off after this treatment. But not only is there a risk of altering the rotation of the terpenes by heating them with sulphurous acid, but adulterated samples will behave in the same way as pure ones, up to a certain point, that is, will give a distillate whose rotation is 8° or 10° higher than that of the original oil. The most satisfactory method is to slowly distil 10 per cent. of the oil from a small fractionating flask. This fraction should have a rotary power not differing from that of the original oil by more than 3°. The *British Pharmacopœia* gives the following limits: Specific gravity, ·857 to ·860; rotation, not below + 59°; the rotation of the first 10 per cent. distilled should not differ by more than 2° from that of the original oil.

The old, and still very common, adulterant of lemon oil is turpentine. When used alone in anything more than very small quantities this is at once detected by the fall in the optical rotation. Or the turpentine can be definitely identified by distilling off the first 10 per cent., when its optical activity will be found to be much different to that of the original oil; or the pinene in the turpentine can be definitely identified by converting it into its crystalline hydrochloride. A little inferior orange oil used to be added to the turpentine, so that the depression produced in the optical rotation by the turpentine, might be counterbalanced by that of the orange oil, which is much higher. But as the boiling point of turpentine is lower than that of either lemon or orange oils, the first fraction of 10 per cent. would contain sufficient turpentine to make its optical rotation differ from that of the original oil (which might be perfectly normal) by more than would be observed in the case of a pure oil. To-day, however, adulterants of a more difficult character to detect are largely employed. These are the waste terpenes produced in the manufacture of "terpeneless" oil of lemons. When one

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remembers that oil of lemons contains 90 per cent. of terpenes it is easily understood that their physical properties do not differ greatly from those of the oil itself. The addition of these terpenes, however, means that the oil contains so much less oxygenated constituents, and to increase these a little lemon-grass citral, or even crude lemon-grass oil is added. Mixtures of this kind are exceedingly difficult to detect, and all the tests of the pharmacopœia can be met by such adulterated samples, if carefully mixed. But if the terpenes—say 90 to 92 per cent.—be distilled off *in vacuo*, the remaining 8 or 10 per cent. will possess a characteristic lemon-grass (verbena) odour, and an indication of adulteration can be obtained by an examination of its optical rotation. Further experiments, however, are necessary before anything more definite can be said about this point. Whilst the grosser adulterations are very easy to detect one is obliged to admit that few oils present so much difficulty to the analyst as a skilfully adulterated lemon oil.

The question of the purity of lemon oil is of vast importance, on account of the fact that such enormous quantities of this oil are imported annually. It comes over in coppers of from 10 lb. to 100 lb., and is used entirely for confectionery and perfumery; in pharmacy its use is entirely for flavouring purposes. Its price varies greatly according to the state of the lemon crop in Sicily, usually varying from 3s. 6d. tc 4s. 6d. per lb. for pure oil, although oils are *offered* as pure al much lower prices.

[*Note*.—A useful paper on the estimation of citral appearec in the *Berichte*, 1898, p. 3324, by Professor Tiemann. He state that citralidene cyanacetic acid C_9H_{15} . CH : C(CN) . COOF is obtained when cyanacetic acid is shaken with citral witl solution of sodium hydroxide. On acidifying, it separate as an oil which soon solidifies and melts at about 90°, c when recrystallised from benzene, at 122°. About 92 t

95 per cent. of the theoretical quantity of the crude acid is obtained, and Tiemann recommends this method for estimating the citral in various oils. In the author's opinion this method is not adapted for the estimation of citral in oils, such as lemon oil, where the quantity present is very small. With lemon-grass oil the results are approximately constant. The results obtained in the latter case are more accurate than those by any other process, but shaking with sodium bisulphite solution gives approximate results, when the citral content is high.]

Oil of Orange.—There are two varieties of ordinary orange oil in commerce, almost identical in composition and properties, but with odours and flavours somewhat different. These are the bitter and sweet orange oils, obtained in the same manner and in the same localities as oil of lemon, from the peel of *Citrus bigaradia* and *Citrus aurantium* respectively. With regard to the origin of the trees, Professor Sadebeck (*Plant Cultivation in the German Colonies, and their Products*) says : "The orange tree is probably indigenous to south-eastern Asia (Cochin China), and thence has spread to the Sunda Islands, further India, Persia, Arabia, Syria, north Africa and southern Europe. Towards the end of the ninth century of the Christian era, it appeared in Arabia, and since A.D. 1002 in Sicily." An oil is prepared by distillation in Jamaica, but it is much inferior in every respect to the expressed oil.

The oil is, in general, produced in the same localities as oil of lemon, but the greater part of it is obtained from Calabria and Messina. The two oils are, chemically, practically indistinguishable, and much of the "bitter" oil, which commands a higher price, is in reality a mixture of the two oils.

The oil consists almost entirely of limonene, as in the case of oil of lemon, but in orange oil *dextro*-limonene

preponderates even more largely than in lemon oil, the optical rotation being correspondingly higher. A little *laevo*-limonene appears to be present, and possibly traces, but only traces, of pinene. The percentage of oxygenated bodies in the oil is very small; indeed, till recently it was customary to describe it as absolutely free from oxygen. However, it is now known to contain a little citral. According to Flatau and Labbé, myristinic acid and myristicol are said to be present in traces. These chemists (*Bull. Soc. Chem.*, Paris [3], xix., p. 361) also state that they identified traces of citronellal and of an aldehyde smelling strongly of orange, but not further examined. They also found a small quantity of an ester present. They state that if 95 per cent. of the oil (terpenes) be removed by distillation, and alcohol added to the remainder, this ester separates in the form of an amorphous powder, and is obtained pure by repeated washing with alcohol. Its melting point is 64° to 65°, and it has a strong orange odour. The chemists above-named consider the ester to be a compound of an unsaturated liquid acid containing 21 atoms of carbon in its molecule. This, however, requires confirmation.

Pure orange oil has a specific gravity ·848 to ·856, but the latter figure is exceptional, from ·848 to ·852 covering most commercial samples. The addition of turpentine or lemon oil only raises this slightly, whilst the addition of alcohol lowers it. The fact that the optical rotation is exceedingly high, renders most adulterants easy to detect. The rotation should fall between + 94° and + 98°, or in the case of the *bitter* oil, as low as + 92° is admissible. Lemon oil or turpentine considerably alter this figure, and are thus easy to detect. As a rule a direct determination of the optical rotation will at once reveal the presence of turpentine, but if necessary the first 10 per cent. may be distilled from a fractionating flask, and the rotation of the fraction observed

In the case of pure oils, this will not differ more than 5° (either above or below) that of the original oil, whereas in the case of oils adulterated with turpentine a considerable variation will be noted. Alterations in temperature have practically the same effect on the rotation of orange oil as on that of lemon oil, but within the limits of the ordinary laboratory temperatures this is quite unimportant. The pure oil commences to boil at 173° to 174°, and about 80 per cent. distils over below 178°. Turpentine and alcohol, of course, lower this temperature. In the present state of our knowledge of the chemistry of this oil, the above physical tests, together with a judgment on the odour in the hands of one accustomed to handle it, are the only criteria of the purity of the oil. Adulteration with the waste terpenes from the manufacture of terpeneless oils of lemon and orange is now resorted to, and, whilst in the former case, the lowering in the optical rotation is as marked as if pure oil of lemon were used, in the latter case detection is very difficult. The terpenes known as "auranciene" possess nearly the same physical properties as orange oil, but are colourless. The effect of adding them to pure orange oil is to impart a light colour and somewhat harsh odour to the oil.

Schimmel & Co. have examined two samples of orange oil from Dominica—which were probably distilled oils. These had the following properties :—

	Specific Gravity.	*Rotation.*
1. Bitter . . .	·853	+ 96° 58′
2. Sweet . . .	·855	+ 95° 57′

They also examined two samples expressed from oranges grown in Florida, U.S.A. Sample No. 1 is from the so-called "sour" orange, believed to be the ordinary sweet orange, grown wild, and thereby deteriorated. Sample No. 2 was from the bitter-sweet orange, probably another deterioration of the same plant. They gave the following results :—

	Specific Gravity.	Rotation.
1. "Sour" . .	·856	+ 94° 15′
2. "Bitter-sweet" . .	·856	+ 96° 25′

The distilled oil of orange owes its inferiority to the effects of heat and steam on the oxygenated constituents, which are of an exceedingly delicate nature.

In addition to the ordinary orange oil, oils of Mandarin and Tangerine oranges are articles of commerce. Occasionally these are met with in a state of purity, but the average sample consists chiefly of ordinary orange oil with a little of the more sweet-scented variety. Mandarin oil is, according to Luca, derived from the fruit of *Citrus bigaradia simensis* and *Citrus bigaradia myrtifolia*. Sawyer calls it *Citrus nobilis*, and Schimmel & Co. describe it as *Citrus madurensis*. It is cultivated largely in China, and the fruit is usually presented to the mandarins, whence its name. It is also cultivated in Malta and the Azores. Luca, so long ago as 1857, investigated the oil (*Comptes Rendus*, 23rd November, 1857) and described it as a liquid of specific gravity ·852 at 10°, boiling at 178°, and having the composition of a terpene. However, it is now certain that the oil contains citral, probably citronellal, and about 1 per cent. of the ester discovered in ordinary orange oil by Flatau and Labbé. The specific gravity of this oil is usually rather higher than that of ordinary orange oil, generally falling between ·852 and ·858. The optical rotation, however, is considerably lower, from + 65° to + 75°.

Oil from Tangerine oranges very closely resembles the above described. The author has examined an undoubtedly pure sample, which had the following properties. Specific gravity, ·8589; optical rotation, + 70° 47′. On exposure to very low temperatures the oil deposited beautiful yellow crystals, which retained their colour after recrystallisation from alcohol. They melted about 70°, but the quantity obtained was too small for further examination.

Oil of Petit-grain.—The original oil of petit-grain was obtained by the distillation of the small unripe orange berry, which, according to Pereira, rapidly underwent decomposition. The petit-grain oil of to-day, however, is distilled from the leaves and young shoots of the bitter and the sweet orange, the former commanding the higher price. According to Sawyer, citrons are usually grafted on to orange stocks, and these stocks during the summer put forth shoots, which are allowed to attain the length of a few feet. They are then pruned off, cut into bundles, and sent to the distiller. The finest oil, as indicated above, is obtained from *Citrus bigaradia.* The best quality oil comes from the south of France, and also from Algeria and the south of Spain. A much less expensive, but still a fine product, comes from Paraguay.

Pure petit-grain oil has a specific gravity ·885 to ·900, and is either laevo-rotary to $-2°$ (European) or dextro-rotary to $+4°$ (South American). It is easily soluble in twice its volume of 80 per cent. alcohol. It contains a high proportion of esters, but as this figure is very variable no limits can well be fixed. Calculated as linalyl acetate, the percentage varies from 50 to 85 per cent., usually about 55 to 60 per cent.

The well-ascertained constituents of the oil are the terpene limonene, linalol, linalyl acetate, geraniol, geranyl acetate, a sesquiterpene, and a stearoptene not yet examined. The oil distilled exclusively from the leaves and buds is, according to Charabot and Pillet, invariably laevo-rotary, and contains a very small quantity of limonene, whereas the South American oil appears to owe its dextro-rotation to a larger percentage of limonene, which may be due to an admixture of small fruits with the distilling material.

Schimmel & Co. have examined an oil distilled from the corresponding parts of the lemon tree, which was termed by its makers "Petit-grain citronnier". The odour resembles that of petit-grain oil, with a secondary odour of lemon. Its

specific gravity was ·869, optical rotation + 34° 11′, and it was far less soluble in alcohol than ordinary petit-grain oil. Citral was detected in it. This was probably mixed with ordinary lemon oil.

An oil distilled from the unripe orange fruits, analagous to the old-fashioned petit-grain oil, is manufactured and offered under the name of "oil of orange peas". Its specific gravity is about ·852 to ·854 and its optical rotation + 75°. It appears to closely resemble ordinary orange oil in composition, although its optical rotation is lower, and its odour is distinctly modified. It contains traces of a pyrrol compound (*Berichte*, 1899, p. 1217). Petit-grain oil is frequently adulterated, chiefly with turpentine, but it is now easy to get pure oil by careful buying. The oil is used extensively in perfumery, especially in the manufacture of *Eau de Cologne*, and is also employed to a considerable extent to adulterate neroli oil with.

Neroli Oil.—This oil is distilled from the fresh flowers of the bitter and the sweet orange. The former, which is the more valuable, is known as "Oil of Neroli, Bigarade," the latter as "Oil of Neroli, Portugal". The greater part of the neroli oil of commerce is distilled in the south of France, one of the chief centres being Vallaurie. The yield of oil varies greatly according to the time of the season when the flowers are collected. The gathering of the flowers commences about the last week in April and continues till the last week in May, or possibly a little later. The early gathered flowers yield about half a gramme of oil per kilo, whilst those gathered late in May yield double this quantity. The petals are separated from the sepals and covered with water in the still, and the contents heated by means of coils of superheated steam. The oil coming over is separated, and the water is sold as orange flower water.

Pure neroli oil has a specific gravity ·870 to ·880, and is

always dextro-rotary, usually about + 4°, but sometimes much higher. On account of the regular adulteration of this oil with both kinds of orange oil, it is probable that rotations of + 20° and higher, which have been recorded, are not at all representative of pure oils; however, it is not easy to fix any definite limits. Again, although no definite limits can be fixed for the ester content, this almost invariably falls between 10 and 20 per cent., calculated as linalyl acetate, and high ester contents should be regarded with great suspicion, as indicative of adulteration with petit-grain oil.

Neroli oil contains limonene, linalol, linalyl acetate, geraniol and one or more paraffin hydrocarbons. None of these bodies, however, are characteristic of the odour of neroli, nor is any one of them responsible for the characteristic fluorescence of the oil. Ernst and Hugo Erdmann (*Berichte*, 1899, p. 1213) have examined the oil, and found that the portion which distils above 115° at a pressure of 10 mm. leaves on saponification a crystalline acid of melting point about 140°. This acid was completely identified as anthranilic acid (*o*-amidobenzoic acid), and it occurs in the oil as its methyl ester. The pure body, methyl-*o*-amidobenzoate, is an oil solidifying at low temperatures in crystals, melting at 24·5° and boiling at 127° at 11 mm. Its specific gravity is 1·163 at 26°. It is easily soluble in dilute mineral acids (on account of its basic character), alcohol or ether, and yields a crystalline hydrochloride. It is strongly fluorescent and has a powerful neroli odour. This body must, therefore, be regarded as the chief odour-bearer of oil of neroli, and artificial neroli oils are now quite easy to prepare. In regard to this discovery, Messrs. Schimmel & Co. claim that they had long known it, and made an artificial oil of neroli oil containing this ester. The crystalline body sold as "nerolin" is β-naphtol-methyl ether. Whether this occurs or not in the natural oil is uncertain.

Schimmel & Co. have distilled a parcel of fresh flowers which they received preserved in salt, and used two methods of preparing the oil. The first portion was distilled with water and the separated oil collected. The water was then redistilled several times and the whole of the oil obtained was mixed together. The second portion was distilled and the water not further treated. In both cases the oil had a specific gravity of over ·870, and both were laevo-rotary (− 0° 52′ and − 0° 40′), whereas French distillates are dextrorotary.

Neroli oil is largely used in perfumery, and is somewhat expensive, fine distillates of the bitter orange flower being worth from 8s. to 10s. per oz., as against 4s. to 5s. for the sweet variety. A large proportion of the oil of commerce is, however, adulterated.

Bergamot Oil.—This oil is obtained from the fresh peel of the fruit of *Citrus bergamia*, the ordinary bergamot. The chief centre of the industry is southern Calabria, which is practically the only province in which the tree is cultivated, extensive plantations being situated at, and in the neighbourhoods of, Reggio, Melito, Gallico, Arangea, Sancta Catarina, S. Lorenzo, Palizzi, Staiti, etc. Almost all the oil is expressed by machines, but as these are usually adjusted for globular fruits, any that have the oblong lemon shape are treated by hand. Hand-pressed oil is, however, rarely met with in commerce. The trees are best grown on well-irrigated, low-lying lands, and are frequently cultivated amongst the lemon and orange trees. The fruit is gathered in the months of November and December and the first week or two in January, when the manufacturing season is over. The resulting oil is of a green colour, due to the presence of chlorophyll (not to the presence of copper, as sometimes stated).

Bergamot oil contains the terpenes limonene and di-

pentene, together with the alcohol linalol and linalyl acetate. To the last-named the characteristic bergamot odour is due, although it is undoubtedly modified by small quantities of one or more bodies, not yet understood. The above-mentioned ester, linalyl acetate, is, then, the body to which attention has recently chiefly been paid. The amount present in the oil varies from about 30 to 42 per cent., although oils with so low a percentage as the first-named figure are to be regarded suspiciously. The soil appears to have a marked influence, as well as the climate, upon this, and, according to Messrs. Schimmel & Co., the amount increases with the ripeness of the fruits. This question, however, requires further investigation. A stearoptene, bergaptene, also occurs in the oil to a small extent, which has the formula $C_{12}H_8O_4$, and melts at 188°. This body is probably a di-oxy-coumarin derivative. According to Crismer, a second solid constituent is present, of unknown composition.

Pure bergamot oil has a specific gravity of ·882 to ·886, and an optical rotation of + 8° to + 20°. Some samples are sufficiently light-coloured to allow their rotation to be observed in a 100 mm. tube, but usually a shorter tube must be used and the rotation calculated. The oil leaves a residue when evaporated on the water bath, which amounts to 4 to 6 per cent. in unadulterated oils. The ester is estimated by a quantitative saponification in the ordinary way, and should yield a result equivalent to at least 35 per cent. calculated as linalyl acetate $C_{10}H_{17}O.OC.CH_3$, although pure samples occasionally contain a little less than this. As the fixed residue obtained on evaporating the oil contains some saponifiable matter, it has been suggested that this also should be quantitatively saponified and the result deducted from the original saponification figure. But as it is not clear what changes occur during the evaporation, it is preferable to

give the results for comparative purposes, on the direct saponification figure, and return the same as linalyl acetate. Pure oils are soluble in half their volume of 90 per cent. alcohol, and usually in twice their volume of 80 per cent. alcohol. In the event, however, of an oil not being entirely soluble in the latter case, as some pure oils are not, the examination of the fixed residue should never be omitted, as any fatty oil, which would decrease the solubility, would be found in the residue, and any excess over 6 per cent. may be regarded as adulteration. A good judgment can be formed on these figures, and, within limits, the value of the oil may be regarded as dependent on its ester percentage.

Rectification, instead of improving, certainly deteriorates bergamot oil. This is due to the fact that the ester is decomposed, so that the percentage of this body falls to 15 or 20 per cent., and the percentage of free linalol increases correspondingly. Of course, rectification removes the green colour, but apart from that, there is nothing to repay the extra trouble and cost.

Amongst the adulterants of bergamot oil, are turpentine, lemon, orange, and fatty oils. The addition of the three first named decrease the specific gravity, solubility and ester percentage; lemon or orange oils raise the rotation. Fatty oils decrease the solubility and increase the residue obtained on evaporation. In addition to these, oil of bergamot of an inferior character is obtained by rasping the peel of the injured small fruit which falls from the tree, and mixing the pulp with water, whereby the oil separates. The residual pulp both of this, and the residue obtained after expressing the oil in the ordinary way from normal fruit, is distilled, and the distilled oil of inferior odour is frequently mixed with the normal oil. This distilled oil is characterised by a low ester percentage, exactly as in the case of rectified oils.

Bergamot oil is employed exclusively in perfumery. Artificially prepared linalyl acetate is an article of commerce, but its price is far higher than that of pure bergamot oil, and its odour, in the author's opinion, much inferior.

Oil of Limes.—This oil is obtained either by an expression process (generally by the ecuelle) or by distillation from *Citrus limetta* (Italian) or *Citrus medica var. acida* (West Indian). The pressed oil is the superior of the two and commands a much higher price. In the south-west of Italy the tree (*Citrus limetta*) is known as *limoncello di Spagna*, and yields its crop of fruit in December and January. For the purpose of manufacturing the oil the green fruit is used, as it then contains more oil than when it is ripe. The juice of this fruit is sweet, whereas that of the West Indian lime is very acid. Italian lime oil, which is expressed, not distilled, is of a brownish yellow colour and has a characteristic fragrant odour of the fruit with a secondary odour of bergamot. Its specific gravity varies from ·870 to ·875, and its rotation from + 56° to + 60°. It contains linalyl acetate to the extent of about 25 per cent., which is responsible for its bergamot odour. It also contains a little free linalol, but not more than 3 or 4 per cent. The bulk of the oil consists of the terpene limonene.

The West Indian oil, which is the usual oil of commerce, is obtained from the fruits of *Citrus medica var. acida*, whose juice contains a large quantity of citric acid. The plant is plentiful in Jamaica, Dominica and Tahiti; but the most important plantations are on the island of Montserrat, one of the Antilles. The lime harvest here lasts from September to January, and the chief product is, of course, the lime juice. An oil is prepared either by pressure or by a process of distillation whilst the juice is concentrating. The distilled oil has a much inferior odour, in comparison with that of the expressed oil. This appears to be due to the partial decomposition of the unstable oxidized constituents

during the distillation, the distillate containing more limonene and having a much coarser odour. The West Indian oil has a different odour to that of the Italian oil, more closely resembling lemon oil. Its specific gravity (expressed oil) is ·873 to ·885, and its rotation + 35° to + 40°. It contains much limonene and some citral. The distilled oil has a lower specific gravity—usually from ·856 to ·868, and an optical rotation of about + 40°. Tilden has found in the semi-solid deposit which is thrown down from crude West Indian lime oil a crystalline substance of the formula $C_{11}H_{10}O_4$, melting at 147°. This body, which has the constitution

$$C_6H_3\left\langle\begin{array}{l}(OCH_3)_2\\ C_3HO_2,\end{array}\right.$$

he terms limettin (*Journ. Chem. Soc. Trans.*, 1890, p. 323, and 1892, p. 344). Oil of limes (or oil of limetta, as the Italian oil is sometimes termed) is largely used as a flavouring agent, for which purpose alone it is employed. A good deal of the cheap so-called lime juice cordial contains no natural lime juice at all, but is merely a solution of citric and tartaric acids, flavoured with oil of limes, or a mixture of this and lemon or orange oils, preserved with sulphurous acid.

Oil of Shaddock.—The shaddock is the fruit of *Citrus decumanum.* It is a large fruit, native to China and Japan, and introduced into the West Indies by Captain Shaddock, whence its name. The oil, which is not known to any extent in commerce, has a specific gravity of about ·860 and an optical rotation of + 90° to + 95°. It is a typical *Citrus* oil, containing much limonene, but its constituents have not yet been carefully examined.

Citron Oil.—This oil is expressed from the fresh peel of the fruit of the true *Citrus medica*, the ordinary citron, a native of the Himalayas, which was cultivated by the Aryans from very early times. In France the fruit is known as a

"cedrat"—the French "citron" being our lemon. Consequently "essence de citrons" must not be confused with citron oil. The tree flourishes in the south of Europe generally, and in Italy, the fruit sometimes weighing from 10 to 14 lb. The oil when pure has a specific gravity about ·860 to ·870, but these limits may be slightly exceeded in either direction. The oil is dextro-rotary, from + 66° to + 76°, and its known constituents are the terpene limonene, and citral—the latter constituent being present to the extent of 4 to 7 per cent.

Oil of Rue.—The herb, *Ruta graveolens*, yields an essential oil characterised by its extremely low specific gravity. The oil is of a pale yellow colour and characteristic odour, and consists almost entirely (at least 90 per cent.) of methyl-nonyl-ketone, $CH_3 . CO . C_9H_{19}$. The specific gravity of the oil varies from ·830 to ·840, and it is always slightly dextro-rotary, from 0° to + 2° 30′. When exposed to the action of a freezing mixture the oil solidifies to a crystalline mass at + 9° to + 10°. It begins to boil at 215°, and is completely distilled at 232°. It should dissolve to a clear solution with from two to three volumes of 70 per cent. alcohol. Pure methyl-nonyl-ketone is a bluish fluorescent oil melting at + 15° and boiling at 225°. The characters above given are sufficient to guard against adulteration, which, however, is frequently practised, the usual adulterant being turpentine and, more rarely, petroleum, which, however, alter the constants of the oil so much as to be very easily detected. Oil of rue is not largely employed in medicine, and has occasionally been employed for illegitimate purposes.

Oil of Buchu.—Several species of *Barosma* are known by the name *Buchu*, and from the leaves of these the oil is distilled. The chief of these are *Barosma serratifolia*, *Barosma betulina* and *Barosma crenulata*. The yield of oil is from 1 to 2 per cent. The specific gravity of the oil, which

possesses a camphoraceous odour, varies from ·940 to ·945, or, occasionally, a little lower, especially in the case of the oil from the leaves of *Barosma betulina*. Flückiger investigated the oil (*Pharm. Jour.* [3], ii., pp. 174 and 219) and stated that it consisted of two main constituents, a solid one, diosphenol, and a liquid one. The former was described by Shimoyama as an aldehyde-phenol, but recent work has thrown some doubt on this. The more recent researches of Kondakoff and Bialobrzeski have proved that the oil contains at least three constituents. These are diosphenol $C_{10}H_{16}O_2$, the chief optically inactive compound in the oil; a hydrocarbon $C_{10}H_{18}$ boiling at 174° to 176°, and a ketone $C_{10}H_{18}O$ which is thus an isomer of menthone, as well as of borneol. Diosphenol is a crystalline solid, melting at 81° and boiling at 232°. It occurs only to a very small extent in the oil distilled from the leaves of *Barosma serratifolia*, whereas that from *Barosma betulina* contains so much that crystals separate at ordinary temperature. The hydrocarbon above referred to is an optically active liquid, $[\alpha]_d = + 60° 40'$, of specific gravity ·866 and boiling at 174° to 176°. It has an odour recalling that of pine leaves. The ketone $C_{10}H_{18}O$ is a slightly laevo-rotary liquid boiling at 206° to 209°, of specific gravity ·902, of agreeable peppermint-like odour. Pure diosphenol can be obtained from the oil by extraction with soda solution and decomposition of the alkaline liquid with an acid, and recrystallising the crude diosphenol from a mixture of alcohol and ether. Buchu oil is often adulterated with turpentine and possibly other oils. It is used to a small extent in medicine.

Angostura Oil.—The bark of *Galipea cusparia* yields between ·5 and 2 per cent. of essential oil. The tree is found in abundance on the mountains in Venezuela, and it is especially plentiful in the country round about the Gulf of Santa Fé. The name *angostura* appears to have

been given to it on account of its having been found first in the district bearing that name, situated on the Orinoco. The oil has a specific gravity ·930 to ·960, and an optical rotation of − 35° to − 50°. It has been investigated by Beckurts and his pupils. In their earlier investigations (*Arch. Pharm.*, ccxxix., p. 591) they obtained 1·5 per cent. of oil from the bark, of specific gravity ·956. More recently (*Arch. Pharm.*, ccxxxv., pp. 518, 634) they obtained the same yield of oil of specific gravity ·941 at 20°, of optical rotation − 50°. The oil decomposes partially, when distilled under ordinary pressure, with the formation of water. A small portion was obtained boiling at 160°, and having an odour resembling pinene. A small quantity of a terpene is thus probably present. The main portion of the oil, however, distils between 260° and 280°, and consists of a sesquiterpene and a sesquiterpene alcohol. The sesquiterpene, which is laevo-rotary, was originally described under the name *galipene*, but has now been shown to be identical with cadinene. The alcohol $C_{15}H_{16}O$ is termed galipol; it is a liquid of specific gravity ·927 at 20°, and is optically inactive. By the action of dehydrating agents this body gives up water and yields cadinene. In addition to these bodies there is also present a small quantity of an inactive sesquiterpene, and traces of a crystalline stearoptene. The oil is used to a small extent, chiefly for the preparation of liqueurs, etc.

Jaborandi Oil.—The leaves of *Pilocarpus pinnatifolius* yield about 5 per cent. of an essential oil, of specific gravity about ·875. Its composition is not well known, but the terpene dipentene has been identified, and also a crystalline hydrocarbon, belonging to one of the unsaturated series. The latter body sometimes occurs to so great an extent that the oil solidifies on cooling.

N. O. ZYGOPHYLLEÆ.

Guaiacum Wood Oil.—This oil is identical with that offered in commerce under the name of champaca wood oil. As a matter of fact neither name can be regarded as correct. The wood is known as *Palo balsamo* or guaiacum wood. It was originally believed to be the product of *Guaiacum officinale*, but it is now clearly settled that it is the product of *Bulnesia sarmienti*, and is known as *Palo santo* (holy wood) to the natives. It appears to be indigenous to Argentine and Paraguay, and is especially plentiful along the course of the river Rio Bermejo, a tributary of the Rio Paraguay. The wood yields from 4 to 8 per cent. of essential oil, which is practically solid at ordinary temperatures. This oil has an exceedingly delicate tea odour, and is well suited both for soap perfumery and for blending with stronger perfumes for ordinary scents. The oil, which is of a hard semi-solid consistency, has a specific gravity of about ·970 at 30°, and is laevo-rotary to the extent of about − 6° to − 8° at its melting point temperature. It liquefies at from + 45° to + 55°, but rapidly solidifies on cooling.

The only constituent yet ascertained has been examined by Wallach and Tuttle. It is a crystalline alcohol of the formula $C_{15}H_{26}O$, which is termed guaiol. This body is identical with that found by Merck and named by him champacol, believing that the wood was really champaca wood. Guaiol melts at 91°, boils at 288° under ordinary pressure, and at 155° under a pressure of 13 mm., and is laevo-rotary. By heating it with zinc chloride, it yields a blue oil, of specific gravity ·910 at 20°, and which appears to be a sesquiterpene. An acetate of the alcohol has been prepared, which boils at 155° under a pressure of 10 mm. In addition to its legitimate use as a perfume, it is now being somewhat extensively used as an adulterant of otto of roses. It is generally mixed with geranium oil, so as to have the sam

congealing point as otto of roses, and is then used under the name "essence de la gaïac à la géranium".

N. O. TEREBINTHACEÆ.

Mastic Oil.—The resin from *Pistacia lentiscus*, the mastic tree, an inhabitant of southern Europe, north Africa and the Levant, which is known as mastic, consists of a mixture of resins and resinoids with about 1 to 2 per cent. of volatile oil. This oil, which has a characteristic, pleasant odour, has a specific gravity of about ·850 to ·870, and an optical rotation of + 20° to + 30°. Its composition is not known, except that it contains one or more terpenes.

Chian Turpentine Oil.—This oil is the product of distillation with water, of Chian turpentine, the resin of *Pistacia terebinthus*, an inhabitant of Syria and the Greek archipelago. The yield is about 15 per cent. of an oil of specific gravity ·860 to ·870, and optical rotation + 10° to + 20°. It resembles turpentine in its composition.

N. O. BURSERACEÆ.

Linaloe Oil.—The linaloe oil of ordinary commerce is distilled both in Mexico and Europe from the wood of several species of *Bursera*, chiefly from *Bursera Delpechiana* and *Bursera aloexylon*, and is in no way connected with aloe wood, as its name implies (*lignaloe*). A linaloe wood is also exported from French Guiana and Brazil, but this, known locally as *bois de rose femelle* or *licari* wood, is the product of one of the *Lauraceæ*, probably *Octea caudata*, and is mentioned here, out of its proper place, as a matter of convenience.

The Mexican wood contains from 7 to 12 per cent. of volatile oil, distributed through the circular strata of woody parenchyma and prosenchyma. It was first investigated by Verneuil and Poisson, who stated that it distilled almost

entirely between 189° and 192°, and that it consisted mainly of an oxygenated body of the formula $2(C_{10}H_8)5H_2O$. Semmler, however (*Berichte*, 1891, p. 207), was the first to discover the true odorous principal of the oil, which he termed linalol. In addition to this alcohol, geraniol and the ketone, methyl-heptenone, have been found in the oil, together with traces of a sesquiterpene and two terpenes. Barbier and Bouveault give as the composition of an oil examined by them :—

Linalol	90 per cent.
Geraniol	2 ,,
Sesquiterpene	3 ,,
Methyl-heptenone	0·1 ,,
Terpene (1)	0·1 ,,
,, (2)	0·1 ,,

The oil is of pleasant odour, referred by some to that of lemon and bergamot, but in the author's opinion not in the least similar to either. It varies in specific gravity from ·875 to ·898, and in optical rotation from − 5° to − 12°. It should be quite soluble in two volumes of 70 per cent. alcohol.

The Cayenne wood has been described under various names, but the researches of Professor Möller have proved that it is the product of one of the *Lauraceæ*, as above mentioned (*Pharm. Post*, 1896, No. 46). The two plants which probably yield the wood are *Octea caudata* and *Licaria guaiaensis*. The oil is obtained to the extent of from 1 to 2 per cent., and is of agreeable odour, and specific gravity ·870 to ·880. It is laevo-rotary − 15° to − 17°, and contains the same principal constituents as the oil from the Mexican wood. Linalol, geraniol and methyl-heptenone have been identified. The oil from the Cayenne wood, however, is not much seen in commerce.

Elemi Oil.—Elemi resin yields from 15 to 30 per cent. of volatile oil. The botanical source of the plant yielding the resin is not definitely decided, but it is probably *Canarium*

commune and other species. Several kinds of elemi, probably of quite different botanical origin, were offered in commerce at one time, but now practically the whole of the resin on the market is the Manila elemi, which in all probability is the product of *Canarium* species. Flückiger and Hanbury state that the oil is colourless, and strongly dextro-rotary, whilst Deville states that the oil is laevo-rotary. This difference is doubtless due to the resin having been obtained from different plants. Schimmel & Co. distilled some oil and found it to have a specific gravity ·900 and to be dextro-rotary. The oil consists chiefly of the terpenes *dextro*-phellandrene and dipentene, but contains also some higher boiling compounds. It has a specific gravity ·870 to ·910, and is dextro-rotary about + 45° (if distilled from Manila elemi). The oil is but seldom employed.

Myrrh Oil.—The resin obtained from *Commiphora abyssinica*, and other species, yields from 2 to 10 per cent. of a volatile oil of specific gravity ·985 to 1·010 and of laevo-rotary power up to − 75°. The chemistry of the oil requires investigation.

Tucholka (*Arch. Pharm.*, ccxxxv., 289) has extracted the essential oil from a Bisabol myrrh coming from the interior of the Somali country, by removing it from the alcoholic solution of the resin by means of petroleum ether. The oil was purified by steam distillation, and then had a light yellow colour, specific gravity ·8836, and optical rotation − 14° 20′. It boiled at 220° to 270°. The yield was 7·8 per cent. By means of dry hydrochloric acid gas, a crystalline hydrochloride was separated, which, on treatment with boiling acetic solution of sodium acetate, set free a hydrocarbon which the above-named investigator terms bisabolene. This hydrocarbon had a specific gravity ·8914 and boiled at 260°. The same chemist suggests the unlikely formula $C_{56}H_{96}O$ for the residual portion of the oil.

Frankincense Oil.—The oil from the resin of various species of *Boswellia*, which is yielded to the extent of 3 to 8 per cent., has a specific gravity ·875 to ·885 and an optical rotation of about − 10°. It consists chiefly of terpenes, of which those identified are pinene, phellandrene and dipentene.

Opoponax Oil.—The resin of *Balsamodendron Kafal* yields from 5 to 10 per cent. of an oil of specific gravity ·860 to ·910 and of very varying optical activity. It contains terpenes, but its chemistry requires investigation.

N. O. Geraniaceæ.

Geranium Oil.—True geranium oil is distilled from the fresh herb of several species of pelargonium, chiefly *Pelargonium odoratissimum*, *Pelargonium capitatum* and *Pelargonium roseum*. As a matter of fact, however, the plants cultivated are varieties of these descriptions, not corresponding exactly with the plant when cultivated true to name in England. The plants are cultivated in open fields in many parts of Algeria, notably at La Trappe de Staoüeli, Castiglione, Sahel, and near Algiers and Constantine. It is also largely cultivated in the south of France, in Spain (chiefly near Valencia and in the province of Almeria), in Italy, Corsica, Réunion, Bourbon and in Provence.

The plants are gathered a short time before the opening of the flowers, when the rose-like odour commences to develop—the leaves at the same time commencing to turn yellow. The odorous oil is contained entirely in the green parts of the plant, the coloured petals being practically odourless. The whole plant is however put into the still, and sometimes rose petals are added, and the resulting fine oil is sold as oil of rose-geranium. There has been much controversy between various chemists regarding the identity and nomenclature of the alcohol contained in geranium oils.

It is not proposed to enter into these controversies here, as an impartial examination of the subject easily enables one to discriminate the facts of the case, but for a succinct account of them, the reader is referred to Schimmel & Co.'s report for April, 1896.

Geranium oil is a sweet-scented liquid of specific gravity ·890 to ·906. It is laevo-rotary, from −6° to −16°. (This oil must not be confused with the so-called Indian geranium oil, the product of one of the Gramineæ, *quod vide*). Pure geranium oil is soluble is three times its volume of 70 per cent. alcohol. The main constituent of the oil is geraniol, but some citronellol is also present. In addition to the free alcohols, the tiglic acid esters are also present, together with small quantities of caproic acid esters. Flatau and Labbé state that two other acids, $C_{14}H_{28}O_2$ and $C_{10}H_{18}O_2$, are also present in the form of esters, but this requires confirmation, and is disputed by Schimmel & Co. Butyric and valerianic oils may also be present in traces. The amount of geraniol (together with the citronellol, calculated as geraniol) present is usually about 60 per cent. in the free state, but sometimes reaches 70 per cent. In addition there is from 15 to 25 per cent. combined in the form of esters. The following table gives the results obtained by Schimmel & Co. for a number of authentic oils :—

	Specific Gravity.	Rotation.	Esters.[1]	Total Geraniol.
			Per cent.	Per cent.
Réunion oil	·890	− 9° 15′	31·3	84·3
" "	·891	− 9°	31·1	84·6
" "	·893	− 8° 32′	33·3	84·9
" "	·891	− 8° 8′	32·5	80
" "	·891	− 8° 57′	34·1	79·3
African "	·898	− 8° 45′	29·1	82·1
Spanish "	·898	− 8° 12′	23·7	85·5
German "	·906	− 16°	27·9	74·1

[1] Calculated as geranyl tiglate.

Schimmel & Co. give the following limits for the various oils :—

	Sp. Gravity.	*Rotation.*
Algerian	·892 to ·900	– 6° 30′ to – 10°
German	·906	– 16°
French	·897 to ·905	– 7° 30′ to – 9° 30′
Réunion	·889 to ·893	– 8° to – 11°

and state that the Algerian variety is poorest in esters, containing from 19 to 29 per cent., calculated as geranyl tiglate, as against 25 to 35 per cent. for other varieties.

Fatty oils and turpentine are frequently added to the pure geranium oil, but these are easily detected by the decrease in the solubility of the oil, besides the alteration in the other constants. Fatty oils also leave a residue on evaporation. Geranium oil is extensively used as a perfume on account of its exquisite odour, and other leaves are sometimes added to the geranium leaves on distillation, in order to produce a still finer product, *e.g.*, rose geranium oil. The geranium oil used so extensively for adulterating otto of roses is not the true geranium oil, but that usually known as Turkish or Indian geranium (*vide supra*).

N. O. Tropæoleæ.

Oil of Tropæolum.—The Nasturtium (*Tropæolum majus*) yields about ·04 per cent. of a strongly smelling essential oil, when the green plant is distilled with steam. The vessel should be well tinned inside, on account of the sulphur contained in the oil. Hofmann investigated this oil in 1874, probably distilling it without previous crushing. In the oil he found benzyl cyanide. Gadamer (*Arch. Pharm.*, 1899, p. 237) distilled the plant, first well minced, with steam, and extracted the small quantity of oil from the distillate with ether. He found that it contained 86 per cent. of benzyl-thiocarbimide. He considers this is due to the fact that there is in the plant an enzyme which decomposes the glucoside present, with the formation of this body. He suggests

that by not crushing the plant the enzyme is destroyed before it can decompose the glucoside which is distributed all through the cells, and that the benzyl cyanide obtained by Hofmann was a product of decomposition of the glucoside through the distillation.

N. O. Meliaceæ.

Oil of Cedrela.—One of the most useful woods in Jamaica is that obtained from *Cedrela odorata*, an immense forest tree. It is a native of the Caribbee Islands and the Barbadoes. Its timber has a pleasant odour of cedar, hence it is frequently spoken of as Jamaica or Honduras cedar, and from the wood most of the ordinary cigar boxes are made. The wood yields from ·5 to 1 per cent. of oil of a light blue colour, of specific gravity ·935, and optical rotation under − 1°. The cedar-wood oils from La Plata and Punta Arenas (Costa Rica), which have been referred to under true cedar-wood oil, are probably obtained from closely related trees of this order. The oil from La Plata is of a light blue colour, has a specific gravity ·928, and is optically inactive. That from Punta Arenas is yellow, of specific gravity ·915 and optical rotation − 6°. It consists chiefly of cadinene.

N. O. Cruciferæ.

Mustard Oil.—The essential oil of mustard is obtained by distilling the seeds of *Sinapis nigra* with water. The oil is official in the *British Pharmacopœia*, which requires it to have a specific gravity of 1·018 to 1·030. The seeds contain the glucoside potassium myronate, which, under the influence of a ferment, myrosin, also present in the seeds, in the presence of water, is decomposed according to the following equation :—

$$\underset{\text{Potassium myronate.}}{C_{10}H_{18}KNO_{10}S_2} = \underset{\text{Glucose.}}{C_6H_{12}O_6} + SO_4KH + \underset{\text{Mustard oil.}}{CS\,.\,N\,.\,C_3H_5}.$$

The chief product of the reaction is thus allyl iso-thiocyanate

(allyl thiocarbimide), a pungent and disagreeable liquid. A small quantity of the normal allyl thiocyanate is also formed, together with traces of cyanallyl and carbon disulphide. The oil is a pungent and unpleasantly smelling liquid of specific gravity 1·015 to 1·030, and optically inactive. As mustard oil consists almost entirely of allyl iso-thiocyanate, and the latter body is easily prepared artificially, there is an artificial oil on the market. This is made by distilling allyl iodide or bromide with alcoholic solution of potassium thiocyanate—a molecular re-arrangement to the iso-thiocyanic radicle taking place. Thus—

$$CN \, . \, SK + C_3H_5I = CS \, . \, N \, . \, C_3H_5 + KI.$$

Pure allyl iso-thiocyanate is a liquid of specific gravity 1·017 at 10°, boiling at 151°.

The artificial oil, however, is not far different in price from the natural oil, and is not official in any pharmacopœia. The amount of allyl iso-thiocyanate present in the oil can be approximately estimated by heating a known quantity with an alcoholic solution of ammonia, when allyl-thio-urea is formed.

The *United States Pharmacopœia* gives the following method for examining the oil. Three grammes of the oil and three grammes of alcohol are shaken in a flask with six grammes of a 10 per cent. solution of ammonia. It should become clear after standing for a few hours, or rapidly if warmed to 50° C., and deposit crystals of allyl-thio-urea (thiosinamine)

$$CS \langle \begin{matrix} NH \, . \, C_3H_5 \\ NH_2. \end{matrix}$$

To determine the quantity, decant the mother liquor and evaporate it slowly on the water bath in a tared capsule, adding fresh portions slowly as the smell of ammonia disappears. Then add the crystals from the flask to those in

the capsule, rinsing the flask with a little alcohol, and heat the capsule on the water bath to a constant weight. Three grammes of oil should yield between 3·25 and 3·5 grammes of thiosinamine, which should melt at 70° (according to the *U. S. P.*). As a matter of fact, the pure compound melts at 74°, and a melting point of 70° to 74° should be obtained. 116 parts of thiosinamine correspond to 99 parts of allyl iso-thiocyanate. Gadamer (*Arch. Pharm.*, 1899, pp. 110, 237) recommends the following process. The mustard oil is dissolved in alcohol to form an exactly 2 per cent. solution. Five c.c. (4·2 grammes) of this solution are allowed to remain with 25 c.c. of decinormal solution of silver nitrate and 5 c.c. of ammonia for 24 hours in a well-stoppered 50 c.c. flask. It is then made up to 50 c.c. with water and filtered from the precipitated silver sulphide; 25 c.c. of the filtrate are mixed with 4 c.c. of nitric acid and a few drops of ferric sulphate solution, and titrated with decinormal ammonium thiocyanate solution, until the characteristic red colour of the ferric thiocyanate appears. From 4·1 to 4·5 c.c. of the solution (corresponding to 1·85 to 2·0 per cent. of allyl thiocyanate in the alcoholic solution) should be required.

White mustard seeds, from *Sinapis alba*, contain the glucoside sinalbin, $C_{30}H_{44}N_2S_2O_{16}$, which on decomposition in the same manner as the glucoside of black mustard yields glucose, sinapine sulphate, and the evil-smelling oil, acrimyl-thiocarbimide (*p*-hydroxy-benzyl-iso-thiocyanate). The reaction takes place as follows:—

$$C_{30}H_{24}N_2S_2O_{16} = C_6H_{12}O_6 + C_{16}H_{23}NO_5 . H_2SO_4 + C_7H_7O . NCS.$$

Acrimyl iso-thiocyanate, or "white mustard oil," is a yellowish oily liquid, of pungent odour and unpleasant hot taste. It is prepared synthetically by treating *p*-hydroxy-benzylamine with carbon disulphide, and the resulting compound with mercuric chloride.

Cochlearia Oil.—Cochlearia or spoonwort oil is distille from the fresh-flowering plant *Cochlearia officinalis* (scurv grass), which yields a very small quantity of the essential oi The specific gravity of the oil is about ·940 to ·955, and it i dextro-rotary to the extent of + 50° or thereabouts. Hofman showed many years ago that the principal constituent wa secondary butyl-iso-thiocyanate, of the formula—

$$CS.NCH\begin{matrix} \diagup C_2H_5 \\ \diagdown CH_3. \end{matrix}$$

Gadamer (*Arch. Pharm.*, 1899, p. 237) has shown that the dried plant without flowers is cut up, and some whit mustard flower is added, the yield of oil is much increase From 28 kilos of the dried plant, which is known as scurv grass, 66 grammes of essential oil were obtained. The o boiled at 150° to 162°, and the bulk of the oil was found t be secondary butyl-iso-thiocyanate. The amount of iso-thic cyanate was estimated by dissolving a weighed quantity c the oil in alcohol, adding excess of decinormal solution c silver nitrate, allowing the whole to remain for 24 hours in well-stoppered bottle, filtering from the precipitated silve sulphide, and titrating the excess of silver with ammoniun thiocyanate solution. The fractions of the oil of highe boiling point (156° to 162°) had a lower specific gravity an higher optical rotation than the earlier fractions. The possibly contained a little limonene.

In order to determine the purity of the oil a quantity ma be heated on the water bath with 10 per cent. of its weigh of ammonia for a few hours under a condenser and the liqui evaporated to dryness. The mass is then extracted wit alcohol and the liquid filtered and evaporated on a watc glass; the resulting crystals of crude secondary butyl-thio urea melt at 125° to 135°. Pure secondary butyl-thio-ure melts at 136° to 137°. An artificial cochlearia oil exists, bu

appears to consist of iso-butyl iso-thiocyanate. The crystalline thiocarbimide yielded by this melts at 93·5°. The usual adulterants can be thus detected, as the thiocarbimides (thioureas) formed from them melt at the following temperatures:—

Allyl (mustard oil)	72° to 74°
Normal butyl	79°
Iso-butyl	93·5°
Tertiary butyl	165°

Horseradish Oil.—The oil of *Cochlearia Armoracia*, which is yielded in very small quantity, contains allyl iso-thiocyanate (mustard oil).

N. O. CISTINEÆ.

Ladanum Oil.—Messrs. Schimmel & Co. distilled a parcel of old ladanum resin, the product of *Cistus creticus*, and obtained therefrom ·9 per cent. of essential oil. *Cistus creticus* is the Cretan rock rose, a native of rocky ground in Macedonia, Thrace, Greece and the islands of Crete, Rhodes, Sicily and Cyprus. Its botanical relationships are hardly decided, as it is regarded by some as being merely a variety of *Cistus villosus* (Linn.). In Cyprus the ladanum (*labdanum*) is chiefly collected by the shepherds from the fleeces of the sheep, who unconsciously collect it from the plants whilst pasturing, the leaves becoming very viscid with the secretion. The oil obtained by Schimmel & Co. had a specific gravity 1·011 and had a fine ambergris odour; after keeping for a few months, crystals to the extent of 25 per cent. were deposited, which have not been thoroughly examined. This oil appears to have been known in the sixteenth century, as a reference is made to it in the *Gross Destillirbuch* by Ryff, published in 1542. An oil has also been distilled from the leaves of *Cistus ladaniferus*, an allied plant, probably a native of Portugal, but very common in Spain. It has a specific gravity ·925.

N. O. Magnoliaceæ.

Champaca Oil.—The so-called champaca wood oil, commonly known as guaiacum wood oil must not be confused with the true champaca oil. The first named is the product of an entirely different plant. The true champaca oil is distilled from the flowers of *Michelia Champaca*, a plant cultivated, and also growing wild, in the forests of the Himalayas, from Nipal and Kumaon eastwards; and also in the Nilghiris and Travancore, Java and the Philippines. The flowers, which are of an exquisite odour, are not unlike a double narcissus. The essential oil distilled from the flowers is known in India as *Pand* or *Champa-ka-utter*. The oil is known as *Yellow Champaca*, whilst that from *Michelia longifolia* is known as *White Champaca*. A sample of the former distilled in Java (yellow champaca oil) was a pale yellow oil of thin consistency, resembling, in a degree, oil of orris in odour. It had a specific gravity ·914, and an optical rotation − 13° 14′. An oil of white champaca from the same source was found to have a specific gravity ·883 and an optical rotation − 12° 50′. Its odour recalled that of basil. According to Schimmel & Co., the specific gravity of the oil from *Michelia champaca* varies from ·907 to ·940 and the optical rotation from − 12° 18′ to − 55°.

Winter's Bark Oil.—The bark of *Drimys Winteri* yields between ·5 and 1 per cent. of this oil. This plant was originally discovered by Captain Winter in the Straits of Magellan, and is now found in various countries from Mexico to Cape Horn. The oil, which has been examined by Avata and Canzoneri, has a specific gravity of about ·945. It consists of a mixture of several bodies from which these chemists state that they have isolated a sesquiterpene. It distilled between 260° and 265° and had a specific gravity ·9344 and a rotary power $[\alpha]_d = + 11° 2'$. They term this body

winterene, but its chemical identity cannot be regarded as settled.

Para-coto bark yields 1·5 per cent. of essential oil. By some this bark has been credited to *Drimys Winteri*, but its botanical origin is not definitely known. According to Wallach and Reindroff, the oil contains the sesquiterpene cadinene, and also methyl eugenol. It has a specific gravity of about 1·02 and a rotation of + 5° 40′. It is completely soluble in 5 volumes of 70 per cent alcohol.

N. O. Resedaceæ.

Mignonette Oil.—The fresh flowers of the mignonette, *Reseda odorata*, yield traces, about ·002 per cent., of an essential oil of exceedingly powerful odour. This oil is semi-solid at ordinary temperatures, and its chemistry is not understood, as the oil is in itself so very rare. Indeed, commercially, an ordinary floral extract is generally used in preference to any direct preparation from the oil. The fresh roots of this plant yield from ·01 to ·04 per cent. of an unpleasantly smelling oil recalling the odour of radishes. This oil contains phenyl-ethyl-thiocarbimide, $C_2H_4(C_6H_5)NSC$, and is a liquid of specific gravity 1·01 to 1·09 and optical rotation about + 1° to + 2°.

N. O. Turneraceæ.

Damiana Oil.—The leaves of various species of *Turnera* (chiefly *Turnera diffusa* and *Turnera aphrodisiaca*) yield about 1 per cent. of oil on distillation. This has a specific gravity ·940 to ·990, and an optical rotation of − 23° to − 25°. It contains a considerable amount of esters, requiring between 4 and 5 per cent. of KOH to saponify it, and deposits, when cooled, a crystalline body, which is probably a paraffin hydrocarbon. The oil finds no employment.

N. O. Clusiaceæ.

Canella-bark Oil.—The bark of *Canella alba* yields from ¾ to 1 per cent. of essential oil. In the drug trade this bark is known frequently as "wild cinnamon," and is found in the south of Florida, the Bahamas, Cuba, Jamaica, Martinique, Barbadoes, etc. The whole tree is very aromatic, especially the flowers, which perfume the neighbourhood for a considerable distance, although they seldom open. The bark is brought to Europe in the form of long quills, rather thicker than those of cinnamon. The taste of the bark somewhat resembles a mixture of cloves and cinnamon, being hot, bitter and aromatic. Meyer and Reiche investigated the oil, of which they obtained ·94 per cent. from the bark, so long ago as 1843, and stated that they isolated four distinct bodies from it. The first was eugenol, the second was described as being closely allied to the principal constituent of oil of cajuput, and the other two were not closely investigated. Flückiger and Hanbury obtained ·74 per cent. of oil from the bark, and stated that it consisted of two parts of an oxygenated body mixed with one part of a hydrocarbon resembling a mixture of mint and cajuput oils. Eugenol, however, remained as the only well-defined body yet ascertained as a constituent of the oil, till 1890, when Schimmel & Co. showed that the body referred to by Meyer and Reiche as resembling the principal constituent of cajuput oil was actually identical with this, being the now well-known cineol. Williams (*Pharm. Rundschau*, 1894, p. 183) has later examined the oil, and has identified pinene and caryophyllene in it. The specific gravity of the oil ranges from ·920 to ·935 and the optical rotation from + 1° to + 3°.

N. O. Dipterocarpeæ.

Gurjun Balsam Oil.—The so-called wood oil or gurjun balsam is the product of several species of *Dipterocarpus*.

This body is an oleoresin, and is used to some extent for adulterating balsam of copaiba. On distillation with water the oleoresin yields from 40 to 70 per cent. of a volatile oil of specific gravity ·920 to ·930 and optical rotation − 35° to − 106°. It contains a sesquiterpene (caryophyllene ?), but its chemistry is not well understood, and requires investigation.

N. O. TERNSTRŒMIACEÆ.

Tea Oil.—According to Müller, the leaves of the tea plant yield from ·6 to 1 per cent. of essential oil. There seems little doubt but that such a large quantity as this must have been obtained from tea artificially scented, but Dr. Van Romburgh has obtained about ·006 per cent. from genuine tea, and found that the chief product of distillation of the leaves was methyl alcohol. Schimmel & Co. have examined samples obtained from partly fermented leaves, and suggest that the oil may be the result of the fermentation process. Two oils had the specific gravities ·866 and ·8557, and were only very faintly optically active. The principal constituent was found to be methyl alcohol, with possibly a little acetone (which were recovered from the watery liquid, not forming a portion of the oil proper). In the oil, methyl salicylate and a body of the formula $C_6H_{12}O$, which appeared to be of an alcoholic nature, were detected. At all events, the latter body yielded compounds with acetic and benzoic acids.

N. O. MALVACEÆ.

Musk Seed Oil.—The seeds of *Hibiscus abelmoschus* yield from ·1 to ·3 per cent. of essential oil of fine odour, known as oil of ambrette, or musk seed oil, having a specific gravity ·900 to ·905, and an optical rotation of 0° to + 1°. It is semi-solid at ordinary temperatures, and probably contains some palmitic acid. A sample of Java distilled oil, however, was liquid at ordinary temperatures, and a French oil of

specific gravity ·908 did not solidify at −10°. This oil requires investigation.

N. O. Ranunculaceæ.

Nigella Oil.—The seeds of *Nigella damascena* yield ·5 per cent. of essential oil of specific gravity ·906. This oil is fluorescent, and has an odour resembling strawberries. Schimmel & Co. have also distilled an oil from the seeds of *Nigella sativa*, which yielded ·46 per cent. of a non-fluorescent oil, of specific gravity ·875, and rotation + 1° 26′. It distilled between 170° and 260° and had an unpleasant odour, not at all resembling that from *Nigella damascena*.

N. O. Anonaceæ.

Oil of Cananga.—Oil of Cananga or Ylang-Ylang oil ("flower of flowers") is the product of distillation of the flowers of *Cananga odorata*, a native of Ava and Tenasserim, and generally distributed and cultivated throughout southern Asia. When wild the tree grows to its maximum height, but its flowers are said to be almost odourless. The cultivation of the plant reaches its highest degree of perfection in the Philippine Islands, and the best variety of the oil is distilled in Manila, where the industry is carried on in a scientific manner. A large quantity of oil also comes from Java and the neighbourhood, but the oil is not nearly of so fine an odour as that from the East Indies. How far this is due to climatic conditions, and how far to the less scientific methods used in the distillation of the oil, is difficult to say. There appears to be very little doubt but that the tree is the same in both cases.

Genuine Ylang-Ylang oil has a specific gravity of ·930 to ·950 (East Indian) or ·910 to ·940 (Javanese). The optical rotation is − 40° to − 45° (East Indian), and − 20° to − 55° (Javanese). The oil is soluble in from ½ to 2 volumes of 95 per

cent. alcohol, and becomes turbid on further addition of alcohol, but without the deposition of oily globules. On steam distillation, a residue of about 5 per cent. is left, so that anything in excess of this figure will probably be a fatty oil—a common adulterant of Ylang-Ylang oil. The decreased solubility in alcohol will also indicate the presence of this adulterant. The earliest investigation of this oil was that of Gal (*Comptes Rendus*, 1873, 16th June), who showed the presence of benzoic acid in the form of esters. Convert (*Arch. du Pharm.*, 1881, p. 218) confirmed the presence of benzoic esters, and also detected acetic acid in the form of esters in the oil. He also considered it probable that there was a small quantity of either an aldehyde or ketone present. Reychler (*Bull. Soc. Chim.*, 1894, pp. 407, 583, 1045) has since shown that linalol and possibly geraniol exist, together with the sesquiterpene cadinene. Pinene, *p*-cresol methyl ether, and a crystalline solid melting at 138°, probably a sesquiterpene alcohol, have also been shown to be present. So that the following bodies, in addition to others not yet identified, have been found in the oil. Pinene, linalol, geraniol, benzoic and acetic esters, cadinene, *p*-cresol methyl ether, and the crystalline body above referred to. Probably other compounds have been identified, as a synthetic oil closely resembling the natural oil is on the market, but the discoverers prefer to keep their work unpublished. East Indian oil appears to have more low-boiling constituents and esters, but less sesquiterpene than the Java oil.

This oil finds a very extensive use in fine perfumery and is somewhat expensive—the East Indian product especially. An exact examination of both varieties of the oil is greatly needed.

For a useful summary of the botanical relationships of this plant, the reader is referred to Sawyer's *Odorographia*

CHAPTER VI.

TERPENELESS OILS.

Of late years the use of essential oils in a concentrated form has become very common. The first attempt in this direction was that of Haensel of Pirna, who in 1876 introduced into commerce his "patent caraway oil". The name "patent" was afterwards changed to "terpeneless," and under this name the majority of the concentrated oils of commerce are now known. Theoretically the whole question is exceedingly simple. Firstly, the terpenes, although bodies possessing distinct odours, cannot be regarded as responsible for the specific odour of a given oil. The characteristic odour-bearer may in almost every case be regarded as one or more oxygenated bodies, usually of higher specific gravity and boiling point, and lower optical rotation than the terpene found accompanying it.

Secondly, although in many cases it appears that the true odour-bearer in an essential oil is the result of either direct or indirect oxidation of a pre-formed terpene in the plant economy, the conditions are so different during the development of the plant, and after the oil is extracted and exposed in the ordinary way to atmospheric influences, that oxidation of the terpene, especially in the presence of light and moisture, causes a serious deterioration of the oil. Added to this is the fact that the terpenes are by far the most insoluble portion of the oil (in alcohol), and we have a scientific basis for the preparation of terpeneless oil. The resulting oil represents the full odour value of a larger bulk

of the original oil, and is deprived of that portion which is not only useless, but even liable to cause deterioration; and is also usually far more soluble in dilute alcohol than the original oil, a matter of considerable importance in several industries.

The above remarks now require qualification. All oils are not fitted for the manufacture of terpeneless oils; or if they are the quantity of terpene present is so small, that it is of no practical advantage to remove it. This will be referred to later.

Whilst the details of the processes of manufacture may vary in different factories, the general principle is identical in all. Advantage is taken of the fact that the terpenes boil at a lower temperature than the odorous oxygenated constituents of the oil. But as heat almost invariably damages the delicate oxygenated bodies, the terpenes are distilled off under a reduced pressure. The lower the pressure, the better for the resulting oil, as liability to change in the oxygenated bodies is rendered less according to the temperature of distillation, which is of course lower as the pressure is less. If the oxygenated constituents of a given oil are so delicate that exposure to this treatment harms them, then there is no justification for the manufacture of a terpeneless oil.

After distilling off the terpenes, or as much of them as possible, the residual oil is treated in various ways according to circumstances.

A terpeneless oil must, for all ordinary purposes, be regarded as the original oil from which it is prepared, merely deprived of its terpenes (except in cases where an admittedly useless constituent other than the terpene is present, such as the traces of stearoptene in lemon oil). This requires emphasising, more especially as, whilst it is generally agreed that some oils owe their characteristic odour to a definite body, the fact is ignored that traces of other bodies not yet

identified, modify the odour into its natural state. Hence the *one* body above referred to, whether isolated from the oil in question, or prepared from some other source, cannot in general truly be described as a terpeneless oil. These pure bodies—such for example as cinnamic aldehyde, citral eugenol, safrol, etc.—should be described as such, and stand upon their merits. In some cases, in the author's opinion, they are preferable to the terpeneless oil, in others they are totally unfit to replace them. These will be referred to in greater detail below. The term "terpeneless oil" was introduced by Haensel in the above sense, and must retain that meaning, in spite of the fact that some manufacturers persist in describing artificial products by this name.

In the manufacture of terpeneless oils, there is naturally a very large accumulation of the terpene. It is customary to name these, not according to their true chemical composition, but after the oil from which they have been prepared Thus the terpene from caraway oil is sold as carvene, tha from lemon oil as citrene, that from orange oil as auranciene although each of these three consists of nearly pure limonen (mostly dextro-limonene). Frequently the unjustifiable nam of "light oil" is given to it; for example, "light oil of cara way," "light oil of camphor," or "light oil of cloves". Th author has examined several of these and found them t consist almost entirely—from 95 per cent. to 99 per cent.—(terpenes merely contaminated with the odour of the oil fro which they had been prepared. They are sold chiefly fc cheap soap perfumery. But if the intelligent soap make compared the perfume of soaps made experimentally wit the ordinary oil and the so-called "light oil," he would fin for example, 1 lb. of genuine oil of cloves produce a far bett result than 25 lb. of the light oil—whilst the price of tl latter is from a quarter to a third of the price of the genuir oil! In addition to this semi-legitimate use of the separat

terpenes, some of them, especially those from oils of lemon and orange, find extensive employment as adulterants of their parent oils. The adulteration of lemon oil, for example, with lemon terpene or citrene is a really serious matter. It is a fact that many tons of this body are prepared every year, and yet it is practically impossible to find it quoted in any list. The author has gone to considerable trouble in the matter, and has had great assistance from numerous commercial sources of unimpeachable standing, and is able to state with certainty that a very considerable proportion of the citrene or lemon terpene manufactured, finds its way back into commerce as oil of lemon, mixed, of course, with a certain proportion of the genuine oil.

In the following notes, only the more important and generally used terpeneless oils will be discussed, as the opportunity for examining these is necessarily limited, and practically every figure given is the result of the author's own analyses.

Terpeneless Oil of Lemon.—This oil is by far the most generally used of all the terpeneless oils, finding extensive employment in the preparation of mineral waters, etc., where solubility in the minimum amount of alcohol is a matter of much importance. The terpeneless oil, when properly manufactured, contains no limonene and very little of the stearoptene of the original oil. This latter body, which is valueless for perfumery or flavouring purposes, separates out to a great extent from the residual oil, after the terpenes have been distilled off. The oil consists of the aldehydes citral and citronellal, together with geranyl acetate, and, in some cases, linalyl acetate, together with small quantities of bodies not yet identified, and which impart to the oil a characteristic sweetness. Genuine terpeneless oil of lemon possesses a specific gravity of ·894 to ·897, and in the author's experience is always laevo-rotary, from -7° to -9°. It is soluble

in all proportions in 90 per cent. alcohol, and in from 5 to 20 volumes of 70 per cent. alcohol. It yields a high proportion to bisulphite of sodium solution—usually from 55 per cent. to 70 per cent., indicating a high proportion of aldehydic constituents. The unabsorbed portion always has a sweet odour—containing geranyl acetate, and a specific gravity of from ·898 to ·905.

In addition to genuine terpeneless oil of lemon, there is on the market an enormous quantity of so-called terpeneless oil, often safeguarded by being called concentrated oil. This is either ordinary oil of lemon from which a portion only of the terpenes have been removed, and which has a low specific gravity and a high dextro-rotation; or it is lemon oil to which a quantity of citral has been added, or in some cases it is practically entirely citral. But as the citral used is obtained from lemon-grass, it usually possesses a more or less marked verbena odour, and, being free from the other oxygenated constituents of lemon oil, is in no sense a good substitute for the true oil. The following figures were obtained from several terpeneless oils obtained from different makers:—

	Specific Gravity.	*Rotation.*
A	·8963	− 7° 21′
B	·8966	− 8° 53′
C	·8966	+ 2° 8′
D	·8707	+ 38° 21′
E	·8698	+ 42° 6′
F	·8712	+ 41° 21′
G	·8836	+ 10° 58′
H	·9036	− 6° 20′
J	·8943	− 1° 41′

Of these the author is able to vouch for the authenticity of samples A, B and C, but in the third of these samples a little terpene appears to have been left in. Samples D, E, F, G contain considerable quantities of terpene, and samples H and J, with marked verbena odour, are manufactured from lemon-grass citral.

The terpene from lemon oil is a mixture of dextro- and laevo-limonene, in which the former largely predominates, and it is this mixture which is sold so largely as "citrene". Its specific gravity is a little lower than that of the oil from which it is distilled, and its optical rotation a little higher.

Terpeneless Oil of Orange.—The constituents of oil of orange are not so well understood as are those of oil of lemon, and, of course, the same applies to the terpeneless oil. All one can say is that the terpene distilled off, which is sold as "auranciene" is principally dextro-limonene, and the residue has a much higher specific gravity and lower optical rotation. Haensel quotes the following figures for genuine oils prepared from the sweet and bitter oils:—

	Specific Gravity.	*Rotation.*
Sweet	·8940	+ 9·65°
Bitter	·8938	+ 5·11°

Whether the oxygenated constituents as a whole are dextro-rotary or not, is hardly certain, but it is clear that the higher the rotation, the greater is the quantity of terpene remaining in the oil. The author has found commercial specimens with much higher rotations than those above quoted, and which clearly contained terpene.

Terpeneless Oil of Caraway.—As caraway oil contains only traces of any other ingredients than the terpene limonene and the ketone carvone, it is clear that terpeneless oil of caraway should approximate very closely to pure carvone in properties. Five samples examined by the author had the following characters:—

	Specific Gravity.	*Rotation.*	*Distilled at*
A	·9637	+ 58° 52′	223° to 224°
B	·9648	+ 58° 30′	224° to 225°
C	·9634	+ 58° 2′	223° to 225°
D	—	+ 55° 34′	—
E	·9619	+ 58° 6′	—

In one case the hydrosulphide $C_{10}H_{14}(OH)(SH)$ and the

oxime $C_{10}H_{14}$: NOH were prepared. The former melted at 184° and the latter at 72° to 73°, with only a single crystallisation. Pure dextro-carvone is usually assigned the following characters :—

Boiling point	223°
Specific gravity	·9598 at 0°
Rotation	+ 62°
Melting point of sulphydrate . .	187°
,, ,, of oxime	72°

The author's experience of the purest carvone which he could obtain, is that the specific gravity here quoted is too low and the rotation too high, and that the figures quoted for the terpeneless oils are more nearly those of the pure ketone.

The terpene distilled off is chiefly dextro-limonene, anc has a specific gravity about ·849 and an optical rotatio + 102°. It is sold under the names "carvene" or light oi of caraway, as it still retains traces of carvone which impar to it a faint but characteristic caraway odour.

Terpeneless Oil of Lavender.—This oil does not contai a very large quantity of terpene, so that the differenc between the terpeneless and the ordinary oil is not nearl so great as the case of the above-described oil. Sample examined by the author had the following characters :—

	Specific Gravity.	*Rotation.*
1.	·897	− 5° 15′
2.	·893	− 5° 3′
3.	.894	− 3° 14′
4.	·904	− 3° 54′

The percentage of esters, estimated as linalyl aceta varies from 30 to 40 per cent., and of free linalol from 18 25 per cent. Sample No. 4 possessed a marked odour bergamot, and it had probably been fortified with artificial prepared linalyl acetate. The most characteristic differen between the ordinary and the terpeneless oils is that tl latter is more soluble in alcohol than the former.

The following figures have been obtained from commercial samples of oil, in whose authenticity the author has every confidence, except in the case of sample (1) of oil of bergamot:—

Terpeneless Oil.	*Specific Gravity.*	*Rotation.*
Lemon grass	·897	− 1° 10′
Bergamot (1)	·9028	− 11° 15′
,, (2)	·8875	− 9° 14′
,, (3)	·8848	− 7° 56′
Limes (expressed)	·8959	− 8° 38′
,, (distilled)	·9202	− 2° 12′
Cloves	1·0720	0°
Geranium	·8959	− 1° 51′
Sassafras	1·088	+ 2°
Juniper	·9157	− 28° 44′
Pimento	1·0623	− 0° 30′
Angelica	·9514	− 3° 48′
Bay	1·034	—
Citronella	·9139	—
Fennel	·982	—
Rosemary	·939	—
Wormwood	·922	—
Ginger	·909	—

Sample No. 1 of terpeneless oil of bergamot probably contained artificial linalyl acetate, and the sample of oil of juniper although apparently free from terpenes, contained much sesquiterpene, as would be expected.

CHAPTER VII.

THE CHEMISTRY OF ARTIFICIAL PERFUMES.

THE present chapter is not intended to deal at large with natural perfumes. This subject is more properly treated in works on materia medica and botany, and the present chapter will be devoted to a purely chemical account of a few well-defined active principles of certain natural perfumes other than essential oils, together with a description of the more important synthetic and artificial perfumes. It is here necessary to draw attention to the fact that by far the larger proportion of artificial perfumes which are quoted in price lists are merely mixtures of a few well-defined bodies; and the majority of fancy names are merely excuses for selling nostrums at excessive prices. The following bodies comprise the more important well-defined artificial perfumes, some of which have necessarily received mention in chapter v.

Vanillin.—This body is the active odorous ingredient of the vanilla pod, in which it occurs to the extent of about 2 per cent., appearing on the surface of the bean as a fine white crystalline efflorescence. It occurs naturally also in Sumatra benzoin (about 1 per cent.), Siam benzoin (·15 per cent.), and the balsams of Tolu and Peru (traces). Numerous other bodies have been recorded as containing it, such as: Asafœtida (Schmidt, *Arch. Pharm.* [3], xxiv., p. 534); beetroot and asparagus (Lippmann, *Berichte,* xviii., p. 3335); the seeds of *Lupinus albus* (Campani, *Chem. Centr.*, 1888, p. 377); the

seeds of *Rosa canina* (Schneegans, *Jour. Pharm.*, 1890, p. 97), etc., etc.

It was first artificially prepared by Tiemann from the glucoside coniferin, which occurs in the cambium of various coniferous woods. The constitution of vanillin is that of methyl protocatechuic aldehyde $C_6H_3(COH)^1(OCH_3)^3(OH)^4$, and coniferin $C_{16}H_{22}O_8 + 2H_2O$, which is a glucoside melting at 185°, was the substance which Tiemann first used for preparing vanillin from, and for whose process Haarmann and Reimer took out a patent. Coniferin was decomposed, either by emulsin or by boiling with dilute acids, into glucose and coniferyl alcohol $C_6H_3(OH)(OCH_3)C_3H_4OH$, and this body on oxidation yields vanillin; or the oxidation may take place first and the hydrolysis afterwards. The process then consisted of the following reactions. When coniferin is oxidised with an aqueous solution of chromic acid it is converted into gluco-vanillin $C_6H_3(O.CH_3)(O.C_6H_{11}O_5)(CHO)$, the glucoside of vanillin, a crystalline body melting at 170°. For this purpose a solution of 10 parts of coniferin in 200 parts of water is treated at the ordinary temperature with a solution of 8 parts of chromic acid dissolved in a small quantity of water, and the mixture allowed to stand for several days. Barium carbonate is then added to precipitate the chromium. The solution is evaporated to a small bulk, treated with alcohol and filtered. The filtrate on evaporation yields crystals of gluco-vanillin, melting at 170°. On treating this body with the ferment emulsin, or by boiling it with dilute mineral acids, it is decomposed into glucose and vanillin. The latter may be extracted with ether.

The most important method, however, by which vanillin is now prepared is by the oxidation of eugenol, the chief constituent of oil of cloves. This process proved the subject-matter of a patent taken out in England in 1876 by Tiemann, and an almost simultaneous one in France by De Laire. The

eugenol was instructed to be separated by diluting the oil with three times its volume of ether and agitating the ethereal solution with a dilute solution of potash or soda. The aqueous liquid is separated and acidified, and the eugenol separated by extraction with ether. The eugenol is first acetylated by means of acetic anhydride, and the resulting acet-eugenol is dissolved in acetic acid and oxidised with permanganate of potassium. The liquid is then filtered, and rendered alkaline, and the whole is then evaporated, and the residue treated with moderately dilute acid, and extracted with ether. The ethereal solution is extracted with a solution of sodium bisulphite, which combines with the vanillin. The double sulphite compound is decomposed with dilute sulphuric acid, and the vanillin is extracted with ether, from which solvent it is obtained in fine white crystals.

The best yield, however, is obtained by first converting the eugenol into iso-eugenol $OH.OCH_3.C_6H_3.CH:CH.CH_3$ by treating it with solution of potassium hydrate. The acetylation product is oxidised, by which acetyl-vanillin is chiefly formed, which yields vanillin by splitting off the acetyl group.

Vanillin is also obtained by starting from meta-amido-benzaldehyde, which is converted into its diazo compound, which yields meta-oxy-benzaldehyde on treatment with water. These reactions may be represented as follows :—

$$C_6H_4\begin{cases} NH_2^{(1)} \\ COH^{(3)} \end{cases} + NOHO + HNO_3 = C_6H_4\begin{cases} N_2.NO_3 \\ COH \end{cases} + 2H_2O$$

Meta-amido-benzaldehyde. *Diazo nitrate.*

$$C_6H_4\begin{cases} N_2.NO_3 \\ COH \end{cases} + H_2O = C_6H_4\begin{cases} OH^{(1)} \\ COH^{(3)} \end{cases} + N_2 + HNO_3$$

Meta-oxybenzaldehyde.

The *meta*-oxybenzaldehyde is then nitrated and methylated, by which means *para*-nitro*meta*-methoxy-benzaldehyde $C_6H_3.NO_2^{(4)}.OCH_3^{(3)}.COH^{(1)}$ is formed. By reduction this

is altered to the corresponding amido-aldehyde, which is again diazotised and the amido-group replaced by hydroxyl in the usual way, when *para*-oxy*meta*-methoxy-benzaldehyde results, which is, of course, identical with vanillin, or protocatechuic aldehyde methyl ether, $C_6H_3 . COH^1 . OCH_3{}^3 . OH^4$. Another complicated method, which is the subject of a patent, is to nitrate *meta*-methoxy-cinnamic acid methyl ester, by which means the corresponding *meta*-methoxy-*para*-nitro-cinnamic methyl ester is formed. This body $C_6H_3.OCH_3{}^{(3)}.NO_2{}^{(4)}.(C_2H_2CO_2CH_3)^{(1)}$ is hydrolysed and the free acid is converted into its ammonium salt, which is dissolved in water and reduced to the corresponding *meta*-methoxy-*para*-amido-cinnamic acid. This is diazotised in the usual way, and the amido group is replaced by hydroxyl, by which means an acid termed ferulic acid is formed. This is *meta*-methoxy-*para*-oxycinnamic acid $C_6H_3(OCH_3)OH . (C_2H_2COOH)$. This acid is oxidised (best as an acetyl compound) with potassium permanganate, and thus converted into vanillin.

There are other methods of obtaining vanillin synthetically, but for fuller details the reader is referred to the various patent specifications of the German Patent Office (D.R.P. 63,007, 63,027, 72,600, 37,075, 33,229).

Vanillin forms fine white needles melting at 81° to 82° and possessing an intense vanilla odour. Some of the cheaper commercial samples are heavily adulterated with the harmless, but odourless body, acetanilide. The effect of this body is to lower the melting point even if present in large quantity, but it is very easily detected, as by boiling with solution of potash, aniline is formed, which is easily detected by any of the usual reactions. A quantitative separation may be effected as follows. The substance is dissolved in ether and the liquid repeatedly shaken with concentrated solution of sodium bisulphite. The vanillin is thus extracted, and the ether, after being washed twice with water is allowed to

evaporate, when the acetanilide remains. This will then be found to have a melting point close to 113°. Benzoic acid and coumarin are also occasional adulterants of vanillin. A little isovanillin $C_6H_3(CHO)^1(OH)^3(OCH_3)^4$ is occasionally present, but this is due to the fact that it is generally formed in small quantity with vanillin, in many reactions. The following figures are of great interest as showing the effect of improved manufacturing processes, advances in chemical discovery, and the opposition of rival patentees. The approximate prices of vanillin per lb. were as follows in the years quoted:—

1876	£160	1888	£16
1877	90	1889	16
1878	56	1890	16
1879	36	1891	15 10s.
1880	36	1892	15 10s.
1881	28	1893	15
1882	23	1894	15
1883	21	1895	13
1884	24	1896	13
1885	17 10s.	1897	2 18s.
1886	16	1898	2 12s.
1887	16		

The following remarks on the use of vanillin are from one of Schimmel & Co.'s reports: "In confectionery and chocolate factories, etc., pure crystalline vanillin can be most advantageously used in the form of a 2½ per cent. vanillin sugar, which weight for weight equals in aroma the best vanilla, and should be used in precisely the same manner. Take of crystallised vanillin 25 gr. (ʒ VI gr. XV), dissolve it in 100 gr. (fl. ʒ IV) of pure, odourless absolute alcohol, pour this solution upon 975 gr. (= 2 lb. 2 oz.) of the finest sugar, and mix it thoroughly in order to distribute it as equally as possible. After having evaporated the alcohol in a warm place, and when the sugar has become thoroughly dry, it should be powdered in an earthenware mortar and sifted.

It is then ready for use, and may be kept an indefinite time without losing aroma. The yellow spots which occur on the sugar after drying are caused by the vanillin.

"This $2\frac{1}{2}$ per cent. vanillin sugar should not be confounded with the vanilla sugar generally used by confectioners. In order to prepare the latter it is only necessary to add to pure sugar as much of the $2\frac{1}{2}$ per cent. vanillin sugar as would otherwise have been taken of the finest vanilla.

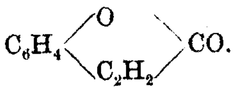
"For liqueur making crystallised vanillin is best used in the form of a $2\frac{1}{2}$ per cent. vanillin essence which, weight for weight, equals the best vanilla in aroma, and is used exactly like it.

"Take of crystallised vanillin 25 gr. (ʒ VI gr. XV), dissolve it in 490 gr. (fl. ℥ XX) of pure absolute alcohol, and add 485 gr. (fl. ℥ XV) of distilled water.

"The vanilla essence generally used for liqueur making is prepared by taking for that purpose as much of the $2\frac{1}{2}$ per cent. vanilla essence as would otherwise have been taken of the finest vanilla.

"For 100 litres (22 gallons) of liqueur 5 grammes (75 gr.) of vanillin, or 200 gr. (= fl. ʒ VII VIJ) of $2\frac{1}{2}$ per cent. vanillin essence are usually employed."

Coumarin $C_9H_6O_2$ is, chemically, the δ-lactone of coumarinic acid, of the constitution—



It is a white crystalline solid, melting at 67° and distilling at 290°. It is soluble in hot water, alcohol, ether, vaseline and oils in general. It is the active odorous ingredient of the Tonquin bean (Tonca or Tonco bean), the seeds of at least two species of *Dipteryx* (N. O. *Leguminosæ*) in which it occurs up to 3 per cent. Coumarin possesses the characteristic odour of the Tonca bean, in which it was discovered

in 1825 by Boullay (*Jour. de Pharm.*, xi., p. 480). It also occurs naturally in abundance in the dried leaves of *Liatris odoratissima* (deer's tongue, hound's tongue), an herbaceous plant common in North Carolina, 1 lb. of leaves yielding from $1\frac{1}{2}$ to $2\frac{1}{2}$ drachms of coumarin. It has also been found in the following plants:—

Angræcum fragrans	*Herniaria glabra*
Myroxylon Pereiræ	*Ruta graveolens*
Ceratopetalum apetalum	*Alyxia stellata*
Ataxia Horsfeldii	*Asperula odorata*
Cinna arundinacea	*Galium trifolium*
Hierochloa alpina	*Liatris spicata*
,, *australis*	*Prunus Mahaleb*
,, *borealis*	*Meliotus officinalis*
Milium effusum	,, *hamatus*
Adiantum pedatum	,, *albus*
,, *peruvianum*	,, *leucanthus*
,, *trapeziforme*	,, *altissimus*
Drynaria Wildenovi	*Ageratum mexicanum*
Phœnix dactylifera	*Copaifera Salikounda*
Aceras Winthrophora	*Trifolium Melilotus*
Nigritella angustifolia	*Anthoxanthum odoratum*
Orchis fusca	

Coumarin was first produced synthetically by Perkin (*Chem. Soc. Journ.*, xxi., pp. 53, 181). He made it by heating salicylic aldehyde $C_6H_4(OH)^1(COH)^2$, acetic anhydride and sodium acetate. The whole solidifies to a crystalline mass, from which, on treatment with water, an oil separates containing coumarin and aceto-coumaric acid. This acid on heating is decomposed into acetic acid and coumarin, so that the product of distillation is principally coumarin.

Coumarin is sometimes adulterated with acetanilide, which should always be looked for; the ease with which it yields aniline, on heating with potash solution, renders it very easy of detection. Some samples, otherwise pure, contain traces of unaltered salicylic aldehyde, which is revealed by the odour.

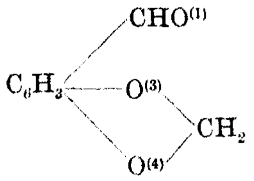
Synthetic coumarin is largely used in the place of Tonca

beans, and forms an extremely useful substance for fixing other odours. Traces of fixed oil are useful in coumarin mixtures, as the coumarin odour appears to become more fixed in this way. Foin coupé, or new mown hay, is a favourite perfume in which coumarin is the chief ingredient. The following table of solubilities of coumarin in alcohol of various strengths and in water has been compiled by Schimmel & Co.:—

100 parts of Alcohol	at 0° C.	at 16-17° C.	at 29-30° C.
Of 90 volume per cent. (dissolve:)	7·1 parts	13·7 parts	42·5 parts
,, 80 ,,	6·0 ,,	12·3 ,,	38·3 ,,
,, 70 ,,	4·4 ,,	9·1 ,,	26·0 ,,
,, 60 ,,	3·2 ,,	6·0 ,,	16·0 ,,
,, 50 ,,	1·7 ,,	3·4 ,,	8·9 ,,
,, 40 ,,	0·7 ,,	1·5 ,,	3·9 ,,
,, 30 ,,	0·3 ,,	0·6 ,,	1·7 ,,
,, 20 ,,	0·2 ,,	0·4 ,,	0·8 ,,
,, 10 ,,	0·15 ,,	0·25 ,,	0·5 ,,
100 parts of water	0·12 ,,	0·18 ,,	0·27 ,,

For further details of the chemistry of coumarin and its allies, the reader should consult any advanced text-book of organic chemistry.

Heliotropin.—This body, also known as piperonal, is a white crystalline compound possessing a powerful odour of heliotrope. It is the methylene ether of protocatechuic aldehyde, of the constitution—



The source from which it was originally made is the base piperine $C_{17}H_{19}NO_3$. Ground pepper, preferably white Singapore pepper (which contains up to 9 per cent. of the alkaloid), is

mixed with slaked lime and water, and the whole evaporated to dryness on a water bath. The dry mass is then extracted with ether, which deposits the piperine on evaporation; or the pepper may be exhausted with alcohol, and the alcohol recovered. The semi-solid residue is mixed with potash solution, and the insoluble powder left is washed with water and recrystallised from alcohol, when the piperine is obtained nearly pure. When boiled with solution of caustic potash in alcohol, the base is converted into potassium piperate, which on oxidation with potassium permanganate yields heliotropin. The heliotropin of commerce, however, is manufactured by the oxidation of safrol. This body (*q.v.*) and its isomer isosafrol yield large quantities of heliotropin on oxidation with potassium permanganate or chromic acid.

To prepare heliotropin from isosafrol (which results from the isomerisation of safrol with alkalies), 5 parts of isosafrol are treated with a solution of 25 parts of potassium bichromate, 38 parts of concentrated sulphuric acid and 80 parts of water. The reaction product is steam distilled and the distillate is extracted with ether and the heliotropin obtained is purified by means of alkaline bisulphite in the usual manner.

Heliotropin melts at 37°, but its perfume is injured by exposure to a temperature several degrees below this, and it should always be stored in cool dark places. In very hot weather the stock may with advantage be kept dissolved in alcohol, ready for use. This perfume is improved by blending it with a little coumarin or vanillin, or with bergamot, lemon or neroli oil. Attention should be drawn to the fact that the fancy perfumes whose names resemble heliotrope are usually mixtures of heliotropin—the cheaper ones being chiefly acetanilide, the more expensive ones containing vanillin or coumarin.

The intelligent perfumer, however, will always prefer to

use the pure definite compound, heliotropin, and mix it according to his taste. In this, as in the case of most synthetic perfumes, fancy names are merely devices by which extra profits may be obtained.

The price of this product per lb. has regularly fallen since it was introduced into commerce. The following table shows the average price since 1880:—

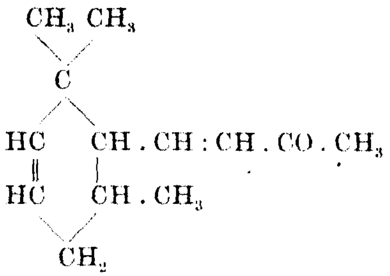
	Per lb.		Per lb.
1880 . . .	£70	1890 . . .	£7
1881 . . .	47	1891 . . .	5 15s.
1882 . . .	31	1892 . . .	4 15s.
1883 . . .	21	1893 . . .	53s.
1884 . . .	21	1894 . . .	43s.
1885 . . .	14	1895 . . .	28s.
1886 . . .	12	1896 . . .	21s.
1887 . . .	11	1897 . . .	17s.
1888 . . .	8 10s.	1898 . . .	16s.
1889 . . .	8		

Aubépine or *Hawthorn*.—The odour of May blossom is fairly well reproduced by anisic aldehyde, and the pure aldehyde should always be purchased, as the various fancy preparations are merely dilutions of this compound. Chemically anisic aldehyde is the methyl ether of *para*-oxybenzaldehyde, of the constitution $C_6H_4(OCH_3)^1(CHO)^4$. It can be prepared from phenol by a series of reactions, or more easily by oxidising aniseed oil. The aldehyde is obtained by gently warming the oil for about an hour with three times its volume of nitric acid (specific gravity 1·1), and separating the heavy oil so formed, and washing it with potash solution. The crude oil is agitated with a warm concentrated solution of sodium bisulphite, with which the aldehyde combines, and the resulting crystalline magma is washed with alcohol and pressed in blotting paper, and dissolved in warm water. Excess of sodium carbonate is added, when the aldehyde is liberated and floats on the surface of the liquid. It can be further purified by distillation. When pure, anisic aldehyde

is a liquid of characteristic hawthorn odour, of specific gravity 1·126 at 15°, boiling at 246° to 248°, and solidifying to a crystalline mass when cooled to a low temperature, melting again at − 4°. By oxidation in the air it is easily changed to anisic acid, which is of no value as a perfume, so that it should be stored in well-filled bottles. It is a very pleasant perfume, and blends exceptionally well with oils of the *Citrus* family, such as orange or petit-grains. It is worth from 25s. to 30s. per lb.

Ionone.—In 1893, after many years of patient research, Tiemann and Krüger succeeded in artificially preparing the artificial violet perfume which they termed ionone. The chemical relationships of this body are so interesting and important that Tiemann's work is here abstracted fairly fully.

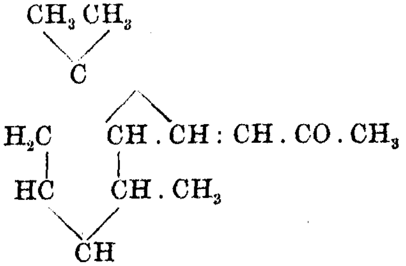
The characteristic fragrance of the violet is also possessed to a considerable extent by dried orris root (iris root), and believing, although apparently erroneously, that both substances owed their perfume to the same body, Tiemann and Krüger used oil of orris for their experiments, instead of oil of violets, of which it was impossible to obtain a sufficient quantity. The root was extracted with ether, the ether recovered, and the residue steam distilled. The non-volatile portion consists chiefly of resin, irigenin, iridic acid and myristic acid, whilst the volatile portion consists of myristic acid and its methyl ester, oleic acid, oleic anhydride, oleic esters, and the characteristic fragrant body which they termed irone. Irone has the formula $C_{13}H_{20}O$, and is an oil scarcely soluble in water, readily so in alcohol, boiling at 144° under a pressure of 16 mm., and of specific gravity ·939 at 20°. Its index of refraction is 1·50113, and it is dextro-rotary. The smell of this oil is quite unlike violets when pure, but if diluted, resembles them fairly closely. It forms a crystalline oxime $C_{13}H_{20}N : OH$ melting at 121·5°. Irone is clearly a methyl ketone, probably of the constitution—



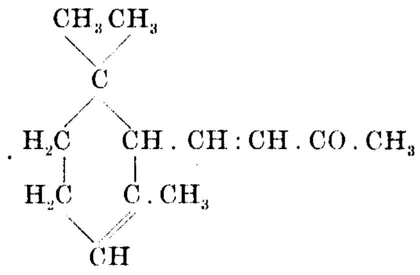
In order to attempt to synthesise irone, experiments were made which finally led to the condensation of citral with acetone, in the presence of alkalies. Irone was not obtained, but an isomer, which Tiemann called pseudo-ionone, as follows:—

$$C_{10}H_{16}O + (CH_3)_2CO = C_{13}H_{20}O + H_2O.$$

Pseudo-ionone is an oil, boiling at 143° to 145° at 12 mm., of specific gravity ·8984, and refractive index 1·53346. If pseudo-ionone be heated with dilute sulphuric acid and a little glycerine or with alkalies, it is converted into another isomeric ketone, the now famous ionone $C_{13}H_{20}O$. This substance boils at 126° to 128° at 12 mm., and has a specific gravity ·9351 and refractive index 1·507, and is optically inactive. It has a characteristic violet odour, and at the same time recalls the vine blossom. Tiemann originally assigned to this body the formula—



But further researches on the chemistry of citral have caused him to now support the formula—



Barbier and Bouveault, however (*Comptes Rendus*, 1897, p. 1308), assign to it the unlikely formula—

$$CH_2 \left\langle \begin{matrix} CH_2\text{—}C(CH_3) \\ CH_2\text{—}C(CH_3)_2 \end{matrix} \right\rangle C \,.\, CH : CH \,.\, CO \,.\, CH_3.$$

Last year Tiemann succeeded in resolving ionone into two structurally identical forms, which he terms *α*-ionone and *β*-ionone. Tiemann and Krüger obtained ionone by heating pseudo-ionone with dilute sulphuric acid. De Laire, using strong acid, obtained a quite similar body, but one which yielded different derivatives. This body is the original *iso*-ionone, or, as it is now called, *β*-ionone. *α*-Ionone is prepared from the commercial product by converting it into the crystalline oxime, which is recrystallised from petroleum, and regenerating the ketone by means of dilute sulphuric acid, when *α*-ionone results. It boils at 123° to 124° at 11 mm., and 134° to 136° at 17 mm. It has a specific gravity ·932 and refractive index 1·4980. The oxime melts at 89° to 90°, and the semi-carbazone at 107° to 108°. *β*-Ionone is obtained from the commercial mixture by means of the semi-carbazone, which crystallises more readily than the corresponding derivative of the *α*-ketone, and can thus be separated. It boils at 127° to 129° at 10 mm., and has a specific gravity ·946 and a refractive index 1·521. The oxime is an oil, and the semi-carbazone melts at 148° to 149°. For further details of the chemistry of

these bodies the original papers should be consulted (*Berichte*, xxvi., p. 2675; xxxi., pp. 808, 867).

The validity of the patent (No. 8736 of 1893) taken out by Tiemann for the preparation of ionone has been attacked on several occasions, but so far always unsuccessfully.

The following is a copy of the provisional and complete specifications provided by the patentee. Further examination of the bodies in question has shown that a few unimportant details require correction:—

Provisional Specification.—I, Johann Carl Wilhelm Ferdinand Tiemann, member of the firm of Haarmann & Reimer, of Holzminden, residing at Berlin, Germany, do hereby declare the nature of this invention to be as follows:—

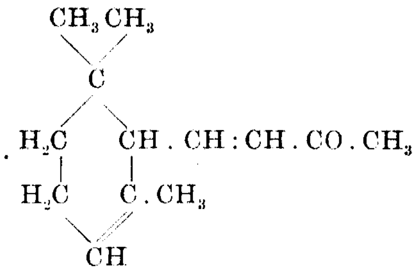
I have found that a mixture of citral and acetone, if it is subjected, in the presence of water, for a sufficiently long time to the action of hydrates of alkaline earths or of hydrates of alkali metals, or of other alkaline agents, is condensed to a ketone of the formula $C_{13}H_{20}O$. This substance, which I term "Pseudo-ionone," may be produced for instance in shaking together for several days equal parts of citral and acetone with a solution of hydrate of barium, and in dissolving the products of this reaction in ether.

The residue of the ether solution is fractionally distilled under a reduced pressure and the fraction is collected, which boils under a pressure of 12 mm. at a temperature of from 138° to 155° C., and from it the unattacked citral and unchanged acetone and volatile products of condensation are separated in a current of steam, which readily carries off these bodies.

The product of condensation remaining in the distilling apparatus is purified by the fractional distillation *in vacuo*. Under a pressure of 12 mm. a liquid distils off at a temperature of from 143° to 145° C. This product of condensation which I term "Pseudo-ionone" is a ketone readily decomposable by the action of alkalies. Its formula is $C_{13}H_{20}O$, its index of refraction is n D = 1·527, and its specific weight 0·904.

The pseudo-ionone has a peculiar but not very pronounced odour; it does not combine with bisulphite of sodium as most of the ketones of the higher series, but, in other respects, it possesses the ordinary characteristic properties of the ketones, forming, in particular, products of condensation with phenylhydrazine, hydroxylamine and other substituted ammonias.

Although the odour of the pseudo-ionone does not appear to render it of great importance for its direct use in perfumery, it is capable of serving as raw material for the production of perfumes, the pseudo-ionone being converted by the action of dilute acids into an isomeric ketone, which I term "Ionone," and which has most valuable properties for perfumery purposes. This conversion may be effected, for example, by heating for several hours in



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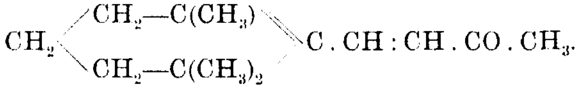

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The following is a copy of the provisional and complete specifications provided by the patentee. Further examination of the bodies in question has shown that a few unimportant details require correction :—

Provisional Specification.—I, Johann Carl Wilhelm Ferdinand Tiemann, member of the firm of Haarmann & Reimer, of Holzminden, residing at Berlin, Germany, do hereby declare the nature of this invention to be as follows :—

I have found that a mixture of citral and acetone, if it is subjected, in the presence of water, for a sufficiently long time to the action of hydrates of alkaline earths or of hydrates of alkali metals, or of other alkaline agents, is condensed to a ketone of the formula $C_{13}H_{20}O$. This substance, which I term "Pseudo-ionone," may be produced for instance in shaking together for several days equal parts of citral and acetone with a solution of hydrate of barium, and in dissolving the products of this reaction in ether.

The residue of the ether solution is fractionally distilled under a reduced pressure and the fraction is collected, which boils under a pressure of 12 mm. at a temperature of from 138° to 155° C., and from it the unattacked citral and unchanged acetone and volatile products of condensation are separated in a current of steam, which readily carries off these bodies.

The product of condensation remaining in the distilling apparatus is purified by the fractional distillation *in vacuo*. Under a pressure of 12 mm. a liquid distils off at a temperature of from 143° to 145° C. This product of condensation which I term "Pseudo-ionone" is a ketone readily decomposable by the action of alkalies. Its formula is $C_{13}H_{20}O$, its index of refraction is n D = 1·527, and its specific weight 0·904.

The pseudo-ionone has a peculiar but not very pronounced odour; it does not combine with bisulphite of sodium as most of the ketones of the higher series, but, in other respects, it possesses the ordinary characteristic properties of the ketones, forming, in particular, products of condensation with phenylhydrazine, hydroxylamine and other substituted ammonias.

Although the odour of the pseudo-ionone does not appear to render it of great importance for its direct use in perfumery, it is capable of serving as raw material for the production of perfumes, the pseudo-ionone being converted by the action of dilute acids into an isomeric ketone, which I term "Ionone," and which has most valuable properties for perfumery purposes. This conversion may be effected, for example, by heating for several hours in

an oil bath 20 parts of "pseudo-ionone" with 100 parts of water, 2·5 parts of sulphuric acid, and 100 parts of glycerine, to the boiling point of the mixture. The product resulting from this reaction is dissolved in ether, the latter is evaporated, and the residue subjected to the fractional distillation *in vacuo*. The fraction distilling under a pressure of 12 mm. at a temperature of from 125° to 135° C. is collected. This product may be still further purified by converting it by means of phenylhydrazine or other substituted ammonias into a ketone condensation product decomposable under the action of dilute acids.

The ketone derivatives of the pseudo-ionone are converted under similar conditions into ketone-derivatives of the ionone. The pure ionone corresponds to the formula $C_{13}H_{20}O$, it boils under a pressure of 12 mm. at a temperature of about 128° C., its specific weight is 0·935, and its index of refraction n D = 1·507.

The ionone has a fresh flower-perfume recalling that of violets and vines, and is peculiarly suitable for being used in perfumery, confectionery and distillery.

The ionone, when subjected at a higher temperature to the action of hydroiodic acid, splits off water and gives a hydrocarbon corresponding to the formula $C_{13}H_{18}$, boiling under a pressure of 12 mm. at a temperature of from 106° to 112° C. This hydrocarbon is converted by strong oxidising agents into an acid of the formula $C_{12}H_{12}O_6$, melting at a temperature of 214° C.

Complete Specification.—I, Johann Carl Wilhelm Ferdinand Tiemann, member of the firm of Haarmann & Reimer, of Holzminden, residing at Berlin, Germany, do hereby declare the nature of this invention, and in what manner the same is to be performed to be particularly described and ascertained in and by the following statement:—

I have found that a mixture of citral and acetone, if it is subjected in the presence of water for a sufficiently long time to the action of hydrates of alkaline earths or of hydrates of alkali metals, or of other alkaline agents, is condensed to a ketone of the formula $C_{13}H_{20}O$. This substance, which I term "Pseudo-ionone," may be produced, for instance, in shaking together for several days equal parts of citral and acetone with a solution of hydrate of barium, and in dissolving the products of this reaction in ether.

The residue of the ether solution is fractionally distilled under a reduced pressure and the fraction is collected, which boils under a pressure of 12 mm. at a temperature of from 138° to 155° C. and from it the unattacked citral and unchanged acetone and volatile products of condensation of acetone by itself are separated in a current of steam, which readily carries off these bodies.

The product of condensation remaining in the distilling apparatus is purified by the fractional distillation *in vacuo*. Under a pressure of 12 mm. a liquid distils off at a temperature of from 143° to 145° C. This product of condensation of citral with acetone, which I term "Pseudo-ionone," is a

ketone readily decomposable by the action of alkalies. Its formula is $C_{13}H_{20}O$, its index of refraction is n D = 1·527, and its specific weight 0·904.

The pseudo-ionone has a peculiar, but not very pronounced odour; it does not combine with bisulphite of sodium as most of the ketones of the higher series, but in other respects it possesses the ordinary characteristic properties of the ketones, forming, in particular, products of condensation with phenylhydrazine, hydroxylamine and other substituted ammonias.

Although the odour of the pseudo-ionone does not appear to render it of great importance for its direct use in perfumery, it is capable of serving as raw material for the production of perfumes, the pseudo-ionone being converted by the action of dilute acids into an isomeric ketone, which I term "Ionone," and which has most valuable properties for perfumery purposes. This conversion may be effected, for example, by heating for several hours in an oil bath 20 parts of "pseudo-ionone" with 100 parts of water, 2·5 parts of sulphuric acid and 100 parts of glycerine, to the boiling point of the mixture.

The product resulting from this reaction is dissolved in ether, the latter is evaporated and the residue subjected to the fractional distillation *in vacuo*. The fraction distilling under a pressure of 12 mm. at a temperature of from 125° to 135° C. is collected. This product may be still further purified by converting it by means of phenylhydrazine or other substituted ammonias into a ketone condensation product decomposable under the action of dilute acids.

The ketone derivatives of the pseudo-ionone are converted under similar conditions into ketone-derivatives of the ionone. The pure ionone corresponds to the formula $C_{13}H_{20}O$, it boils under a pressure of 12 mm. at a temperature of about 128° C., its specific weight is 0·935, and its index of refraction n D = 1·507.

The ionone has a fresh flower-perfume recalling that of violets and vines, and is peculiarly suitable for being used in perfumery, confectionery and distillery.

The ionone, when subjected at a temperature surpassing 100° C. to the action of hydroiodic acid, splits off water and gives a hydrocarbon corresponding to the formula $C_{13}H_{18}$, boiling under a pressure of 12 mm. at a temperature from 106° to 112° C. This hydrocarbon is converted by strong oxidising agents into an acid of the formula $C_{12}H_{12}O_6$ melting at a temperature of 214° C.

Having now particularly described and ascertained the nature of this invention, and in what manner the same is to be performed, I declare that what I claim is:—

1. A new chemical product termed pseudo-ionone obtained by the reaction of citral upon acetone in the presence of alkaline agents and subsequent treatment of the products, substantially as described.

2. A new article of manufacture termed ionone suitable for perfumery and the like and having the characteristics hereinbefore set forth, obtained from pseudo-ionone referred to in the preceding claim, substantially as described.

3. The process for the production of the pseudo-ionone referred to in the first claim, consisting in the subjection of a mixture of citral and acetone to the action of an alkaline agent, and in purifying the product of this reaction, extracted by means of ether, by fractional distillation, substantially as described.

4. The process for the production of the ionone referred to in the second claim, consisting in treating the pseudo-ionone referred to in the first claim or its ketone condensation products with phenylhydrazine or other ammonia derivatives, finally with acids, substantially as described.

The commercial product, as put on to the market, is a 10 per cent. solution of ionone in alcohol. This is due not only to the expensive nature of the product, but also to the fact that its odour is very intense, and when pure, not like that of violets. Ten grammes of this solution are sufficient to produce one kilo of triple extract of violets when diluted with pure spirit. The perfume is improved both for extracts and soaps by the addition of a little orris oil, but in the author's opinion the odour of ionone is not nearly so delicate as that of the natural violet, although far more powerful. The prices asked for it are very high, and in regard to this the following optimistic statement occurs in Messrs. Schimmel & Co's. report for October, 1894: "The opinion, which is frequently expressed, that the price of ionone solution will probably be reduced before long is not justified. It is not the intention of the manufacturers to depreciate the article without reason or necessity, a policy which can only meet with the approval of the maker of high class perfumes, for whose use ionone is intended, and who cannot gain by seeing violet odour, like so many other preparations, brought down to the level of a vulgar scent for common people." The experiences of vanillin, coumarin, heliotroprin and other synthetic perfumes have not been so, and time alone can show whether ionone will prove an exception to this rule.

There are many fancy violet perfumes offered in the market under various names, but they are as a rule merely

dilutions of ionone with a little orris oil, and sometimes a little artificial musk.

With regard to the practical use of ionone, which sometimes presents a difficulty to perfumers, Messrs. Schimmel & Co. write:—

"This beautiful article maintains its position in the front rank of preparations for perfumery, and will probably remain without a rival among artificial perfumes for some time to come. Although the violet scent has long been a favourite perfume, its popularity has doubled through the invention of ionone, and it is not too much to say that the introduction of that body alone has made it possible to produce a perfect extract. Some of the leading European perfumers produce violet extracts which may be recommended as examples of excellence, and which have deservedly become commercial articles of the first importance. The inventors of ionone have earned the gratitude of the entire perfumery industry, and may be congratulated in turn upon the remarkable success of their invention.

"As we have already pointed out on a previous occasion, the preparation of a violet extract in which ionone is made to occupy its due position is not such an easy task as is often assumed; on the contrary, it requires a long and thorough application.

"To obtain a perfect result with ionone is an art in the true meaning of the word, and on that account no inexperienced hand should attempt it. We again and again lay stress upon this fact, because in our business we are constantly brought face to face with people who think that they can make a suitable violet extract by simply mixing alcohol with ionone solution. This view is quite wrong. The employment of ionone presupposes above everything else that the user is acquainted with the peculiarities of the article and knows how to deal with them. Again and again the

uninitiated come to us with the complaint that ionone has no odour at all, or that it smells disagreeably, although as a matter of fact these objections are usually withdrawn upon closer acquaintance with the article. The assumptions in question are only due to a blunting of the olfactory nerves, or, more correctly, to a nasal delusion, which also occurs sometimes in the case of other flower odours and to which people are known to be particularly liable when smelling freshly gathered violets.

"The principal thing in connection with the employment of ionone is to discover its proper degree of dilution. In its natural state the body is so highly concentrated as scarcely to remind one of violets. This is the reason why it was placed in trade in the form of a 10 per cent. solution, and not in its pure state. This form has proved an exceedingly useful one. In using it for extracts, powders, sachets, etc., the solution must be further diluted and fixed with some orris oil, civet and musk."

By using acetone homologues, or by replacing the citral with citronellal, homologous or reduced ionones are produced respectively, which have intense odours of a similar character.

The above remarks apply to the commercial product. known as ionone. There is, however, another patent in existence for the preparation of artificial violet oil, taken out in 1896 by Fritzsche & Co. of Hamburg (No. 26, 350), which up to the present does not appear to have been contested. The complete specification of this patent reads as follows :—

I, Alfred Julius Boult, of 111 Hatton Garden, in the County of Middlesex, Chartered Patent Agent, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement :—

This invention relates to a process for manufacturing hitherto unknown oils having a violet scent.

Patents No. 8736 of 1st May, 1893, and No. 17,539 of 18th September, 1893, describe the manufacture of ionone, which is an essential oil, boiling at 128°

under 12 mm. pressure, and of specific gravity of 0·935. This oil is optically inactive.

The final product of the process according to the present invention is an oil boiling at 142° to 150° C. under 12 mm. pressure and of specific gravity of from 0·94 to 0·95. It differs from ionone by having when concentrated a very strong scent similar to that of sandalwood by producing a left-handed rotation of a polarised ray and by having when diluted a scent more closely approaching that of natural violets than does that of ionone.

Analysis shows that this oil consists of several ketones of the group $C_{13}H_{20}O$ of higher boiling points and greater density than those of ionone. These ketones are optically active, and both their existence and their artificial production have been hitherto unknown.

The process employed in carrying out this invention is as follows: A mixture of 1 to 1¼ parts acetone (45 kg.), 1 part of lemon-grass oil (38 kg.), 1½ to 2 parts of alcohol (75 kg.), 1 to 2 parts of a concentrated lime-free solution of chloride of lime (75 kg.), to which is added a little of cobaltous nitrate (30 gr.) dissolved in water, is boiled during 6 to 18 hours at a temperature of 70° to 80° C. in a reflux cooling apparatus.

The alcohol and the excess of acetone are first distilled off and then an essential oil is obtained, which, after the first distilled portion (about 4 kg.) of specific gravity 0·88 has been removed, represents the stuff for producing artificial oil of violets. It is an essential oil with a boiling point of 155° to 175° at 12 mm. pressure (about 25 kg.).

This oil is heated at 110° C. with a solution of bisulphate of sodium of 11° Beaume (42 kg. for 360 litres of water) in a vessel with a mixing device until the samples distilled every day show that the first running, which has an unpleasant smell, has reached the density of 0·936. This happens after about 8 days (the first running being about 8 kg.).

The crude product (about 17 kg.) in the vessel is then purified by fractional distillation, all the bad-smelling parts being removed, so that finally there remains an oil of a density of 0·948 to 0·952 (15° C.) boiling at 142° to 150° C. under 12 mm. pressure.

The lightest portion of this oil has a specific gravity of 0·945 and boils at 142° C. under 12 mm. pressure; the largest portion of it, which has the pleasantest and strongest smell, boils at 149° C. and has a specific gravity of 0·953. Analysis has shown that both substances belong to the group of ketones $C_{13}H_{20}O$.

By using other ketones instead of acetone homologous substances may be obtained.

The product obtained by the above described process contains no ionone, for it contains no ingredient boiling at 128° C. under the pressure of 12 mm. and having a specific gravity of 0·935. The violet-like smell of the product obtained according to the present invention is the result of the presence of substances which are different from ionone, as their specific gravity and their boiling point are higher than those of ionone. The new product has the advantage that it can be manufactured in a very simple and economical

manner, and as its smell is much more like that of real violets than is the smell of ionone, and as it is more constant and less volatile than ionone, it is much more suitable for artificial violet scent than the "ionone" which has hitherto been the only artificially made substance known for this purpose, and which is much more difficult to manufacture.

Having now particularly described and ascertained the nature of the said invention as communicated to me by my foreign correspondents and in what manner the same is to be performed, I wish it to be understood that I do not claim anything described and claimed in the Specifications of Letters Patent Nos. 8736 and 17,539, A.D. 1893, granted to Johann Carl Wilhelm Ferdinand Tiemann, but I declare that what I claim is :—

1. *As an article of manufacture an essential oil having the smell of* violets boiling at 142° to 150° C. under a pressure of 12 mm. and of a specific gravity of 0·948 to 0·952 (15° C.).

2. A process for the manufacture of hitherto unknown oils having the smell of violets, which oils have a higher boiling point and higher specific gravity than ionone.

3. A process for the manufacture of hitherto unknown oils boiling at 155° to 175° C. under the pressure of 12 mm., which can be converted into violet-smelling oils of higher specific gravity and higher boiling point than those of ionone by being boiled with different substances, such, for instance, as bisulphate of sodium.

4. The manufacture of homologous substances by using other ketones instead of acetone.

5. A process for the manufacture of artificial essence of violets consisting in causing lemon-grass oil, alcohol, acetone, and concentrated solutions of salts of hypochlorous acid to react on one another at the boiling temperature.

6. Process for manufacture of artificial essence of violets consisting in causing lemon-grass oil, alcohol, acetone, and concentrated solutions of salts of hypochlorous acid to react on one another at a boiling temperature, cobaltous nitrate being added if desired.

The author is indebted to Messrs. Fritzsche & Co. for the following information, which is given on their authority and responsibility.

They state that their invention relates to the preparation of cyclic ketones of the same group as ionone, but with higher boiling points and higher specific gravity. They claim to have proved that, corresponding to the pseudo-ionone of the patent No. 8736 of 1893, which distils at 143° to 145° (12 mm.), and which finally gives the ketone ionone of boiling point 126° to 128° (12 mm.), and specific gravity 0·935 (20° C.), there exists

also an iso-pseudo-ionone which distils at 149° to 151° (12 mm.), and which gives iso-ionone of boiling point 133° to 135° (12 mm.) and specific gravity 0·943 (20° C.), and further that there exists still another iso-pseudo-ionone which distils at 157° to 160° (12 mm.), and which gives a cyclic ketone of boiling point 142° to 146° and specific gravity 0·960 (20° C.).

They also claim that large quantities of iso-pseudo-ionone are formed in the process of Tiemann's patent, and which can be separated by distillation, coming over at a higher temperature than the ordinary pseudo-ionone. As the ionone litigation may be prolonged for some time, it is inadvisable to discuss these points for the present at any greater length.

Artificial Musk.—The chemistry of natural musk, the preputial secretion of the musk deer, *Moschus moschiferus*, is quite unknown, and attempts to prepare artificial musk have not been made on the basis of any knowledge of the constitution of the natural perfume. For accounts of the materia medica and commerce of this natural product, works on materia medica should be consulted. A useful account will be found in vol. i. of Sawyer's *Odorographia*.

For many years attempts have been made to artificially imitate the odour of musk. To a certain extent successful experiments were made by Margraff and Elsner (*Journ. für Praktische Chemie*, 1842). Rough pieces of amber, ground to powder and mixed with sand, are distilled in an iron retort, the oil which distils over is separated from the fœtid liquor and succinic acid which accompanies it, and after being rectified at a gentle heat with about six times its volume of water, is gradually added to and digested with 3¼ parts by weight of fuming nitric acid, artificial cold being employed to prevent any portion of the oil carbonising. A resinous matter of a yellowish colour forms, which, after being dried, is the product which is required. It is said to be also formed by digesting for ten days an ounce of fœtid

animal oil, obtained by distillation, and half an ounce of nitric acid, then adding a pint of rectified spirit, and digesting for one month. Another artificial musk has been patented in England (No. 18,521, 18th Dec., 1888) by Schnaufer & Hupfeld, of Frankfurt. The specification of this patent states that "three parts of metaxylol, two parts of isobutyl alcohol, and nine parts of chloride of zinc are heated in a digestor to from 220° to 240°, until the pressure, which at the commencement is from 25 to 29 atmospheres, sinks to below 6 atmospheres. The resulting hydrocarbon, corresponding to the formula $C_{12}H_{18}$, is collected, and the fraction which distils over at from 190° to 230° is nitrated with HNO_3, or with HNO_3 and H_2SO_4, whilst being cooled. The product of the reaction is poured into water, whereupon a reddish-brown oil separates, which is washed several times with alkaline water. The formula of this oil is $C_{12}H_{17}NO_2$, and in a concentrated condition it possesses a sweet smell, whilst in a dilute solution it gives off a penetrating and enduring musk-like odour."

The complete specification states that "aromatic hydrocarbons containing the iso-propyl, iso-butyl, or iso-amyl group, on treatment with fuming nitric acid or a mixture of strong nitric acid (40° to 44° B.) and sulphuric acid (66° B.), produce derivatives which, in very dilute alcoholic solution, furnish a liquid possessing an odour resembling tincture of musk in the highest degree". Only one example of the process is given in the provisional specification, but of course the process may be carried out with the other well-known homologues. "The hydrocarbons may be produced in the ordinary way, but we produce them by the following operation. Toluene or xylol is heated in a digestor with iso-propyl or iso-butyl, or iso-amyl alcohol in molecular quantities, with the addition of from four to five times the quantity of chloride of zinc, to the boiling point of the hydrocarbon, or to about 40° or 50° above

the boiling point of alcohol, until the pressure, which at the commencement was equal to about 26 atmospheres, sinks to a little above 2 or 3 atmospheres. The product of the reaction is subjected to fractional distillation.

"By the above process the following hydrocarbons are obtained :—

1. From Toluene :—
   Methylisopropyl-benzene.
   Methylisobutyl- ,,
   Methylisoamyl- ,,
2. From Xylol :—
   Dimethylisopropyl-benzene.
   Dimethylisobutyl- ,,
   Dimethylisoamyl- ,,

"To produce the 'musk-substitute' :—

"We add to the above-mentioned hydrocarbons, which during the operation should be kept thoroughly cool, a little *more than the molecular quantity of fuming nitric acid or* nitro-sulphuric acid. The acid should be gradually run in and the whole then allowed to stand undisturbed for from one to two hours, the resulting mass being then poured into water in order to get rid of the excess of acid. The well-washed substances thus obtained are then subjected to distillation by means of steam, whereupon simultaneously formed bodies, which smell like nitro-benzol and overpower the musk odour, readily distil over, whilst the pure substances remain behind."

The artificial musk which to-day is practically the only one used is that manufactured under the patent of Albert Baur (English patent No. 4963 of 1889). The provisional and complete specifications of this patent are as follows :—

Provisional Specification.—I, Albert Baur of Gispersleben, in the Empire of Germany, Doctor, do hereby declare the nature of this invention to be as follows :—

The object of this invention is to produce a compound or material, or series of compounds or materials, having the properties of musk.

To this end I purpose to make a nitrated hydrocarbon of the $C_{11}H_{16}$ group and proceed as follows :—

Toluene is mixed with a haloid combination of butane and boiled with addition of chloride or bromide of aluminium. Water is added to the product and it is then distilled with steam, and that portion which distils over at a temperature between 170° and 200° C. is taken and treated with fuming nitric acid and fuming sulphuric acid. The resulting product is washed with water and crystallised from alcohol.

The product may be dissolved in alcohol, and on addition of a small quantity of ammonia or sal-ammoniac will exhibit all the essential properties of a tincture of musk.

Complete Specification.—I, Albert Baur of Gispersleben, in the Empire of Germany, Doctor, do hereby declare the nature of my invention and in what manner the same is to be performed to be particularly described and ascertained in and by the following statement :—

The object of this invention is to produce a compound or material, or series of compounds or materials, having the properties of musk.

To this end I make a nitrated hydrocarbon of the $C_{11}H_{16}$ group and proceed as follows : –

Toluene is mixed with a haloid combination of butane and boiled with addition of chloride or bromide of aluminium. Water is added to the product and it is then distilled with steam, and that portion which distils over at a temperature between 170° and 200° C. is taken and treated with fuming nitric acid and fuming sulphuric acid. The resulting product is washed with water and crystallised from alcohol.

The product may be dissolved in alcohol, and on addition of a small quantity of ammonia or sal-ammoniac will exhibit all the essential properties of a tincture of musk.

For carrying the invention into practice, five parts of toluene are mixed with one part of butyl bromide, or butyl chloride or butyl iodide, and to these may be added gradually whilst boiling $\frac{1}{5}$ part of aluminium chloride or aluminium bromide ; this results in the development of hydrobromic acid, or hydrochloric acid or hydriodic acid respectively, and a product of reaction is obtained from which by the action of steam the hydrocarbon $C_{11}H_{16}$ and unchanged toluene are distilled. By the admission of steam the hydrocarbon is carried along and may be obtained in a condenser as a colourless oil floating on the water. The oil removed and dried by means of chloride of calcium is fractionated, and in this manner the necessary hydrocarbon for the production of artificial musk is obtained, 100 parts of the former giving a like quantity of musk preparation. Three parts of fuming nitric acid of 1·52 specific weight and six parts of fuming sulphuric acid are mixed together, and to this mixture is carefully added whilst cooling one part of the hydrocarbon aforesaid. Each drop causes a violent reaction. As soon as all the hydrocarbon is added, the whole mixture is heated up to a temperature of about 100° C. After cooling, the nitro product is precipitated by pouring into cold water of about five to six times the volume, and is separated from

superfluous acid by washing with cold water. The nitro product separates first as a heavy viscid oil, which after some time hardens into a firm crystalline substance.

The raw nitro product is then purified by recrystallisation from alcohol of 90 per cent. strength. The purified product crystallises out in yellowish-white needles, possessing a strong smell of musk.

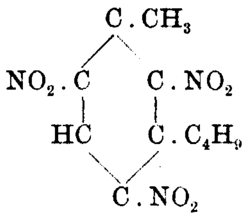
Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

The process for producing artificial musk substantially as described.

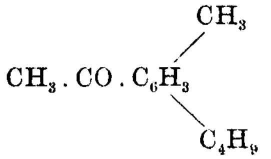
The original scientific account of the preparation of this body stated (*Comptes Rendus*, cxi., p. 238) that *meta*-isobutyl toluene was heated on a water bath for twenty-four hours, with five times its weight of a mixture of sulphuric and nitric acids. The product was subjected to a repetition of the same treatment, so as to convert it into trinitro-butyl toluene, which crystallises from alcohol in white needles melting at 96° to 97°. It is insoluble in water, but soluble in organic solvents. Even in very dilute solutions this compound has a strong odour of musk, and for many purposes can replace the natural product. The homologues of isobutyl toluene behave similarly and trinitro-isobutyl metaxylene has an exactly similar odour. In a later communication (*Berichte*, xxiv., p. 2832) Baur stated that his previous view was incorrect, and that the "artificial musk" was the trinitro-derivative of *tertiary* butyl xylene, and not of isobutyl xylene, owing to the occurrence of an intra-molecular change during the reaction. Tertiary butyl xylene is easily prepared by the interaction of tertiary butyl chloride and toluene in the presence of aluminium chloride as follows:—

$$C_4H_9Cl + C_6H_5 . CH_3 = C_4H_9 . C_6H_4 . CH_3 + HCl.$$

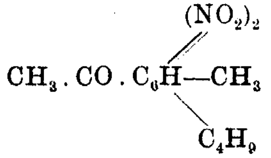
The mono- and dinitro products have no musk odour, and therefore the nitration of the hydrocarbon should be carried as far as possible. The constitution of this artificial musk, or "musk Baur" as it is often called, is probably—



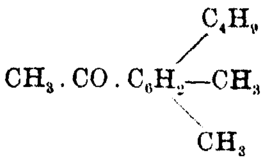
Still later (*Berichte*, xxxi., p. 1344), Baur has shown that if an acetyl group is introduced into the butyl toluene molecule, and the methyl ketone thus formed is nitrated, artificial musk (ketone musk) is produced. One part of butyl toluene, ten parts of carbon disulphide, and six parts of aluminium chloride are cooled in a flask and six parts of acetyl chloride are run in quickly. After distillation on a water bath, the residue is poured on to ice and treated in the usual manner. The acetyl derivative is obtained as an oil with a pleasant aromatic odour, boiling at 255° to 258°, of the formula—



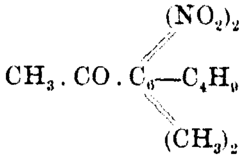
By nitrating this ketone a dinitro-derivative—



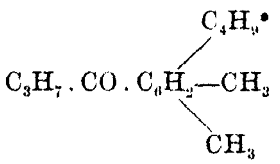
is obtained in needles melting at 131°, and having a strong musk odour. In this compound one of the nitro groups of the original artificial musk, trinitro-butyl toluene, has been replaced by the acetyl group. Which group has been so replaced is uncertain. A quite similar body is obtained from butyl xylene, the resulting ketone—



melting at 48°, and yielding a dinitro derivative—



melting at 136°, and having a strong musk odour. Instead of using acetyl chloride, either butyryl chloride or valeryl chloride may be used, and higher homologues produced. Butyl-xylyl-propyl ketone—



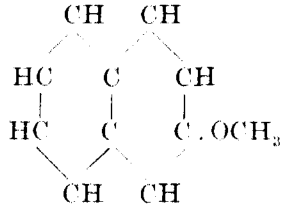
melts at 50° and boils at 290°. It forms a dinitro derivative, melting at 128°, with a powerful musk odour. The corresponding butyl-xylyl-butyl ketone is an oil boiling at 185° to 190° at 14 mm., and its dinitro derivative melts at 151°, and has also a powerful musk odour. An error occurs in the abstracts of this paper in the *Chemical Society's Journal* (1898, p. 525), where the propyl and butyl groups have been rendered butyl and amyl respectively.

The artificial musk of commerce contains the nitrated hydrocarbon as its odorous constituent.

The use of artificial musk is fairly extensive for perfumery of a certain kind, where powerful odours are desired. It finds considerable employment in the scenting of toilet soaps, a little alkali improving its odour.

Artificial Neroli.—There are two artificial neroli substitutes which are more or less common commercial articles. One of these is a crystalline product sold under the name of nerolin at about 1s. 6d. per ounce, whilst the other is a "synthetic neroli oil," sold at about 6s. per ounce.

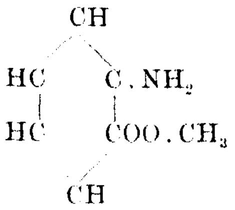
Nerolin crystals should be of a definite character, as this body is expected to be the pure compound—β-naphtol methyl ether, of the constitution—



This body is a white crystalline compound, melting at 70° and boiling at 294°. It can be prepared by heating 5 parts of β-naphtol with 5 parts of pure methyl alcohol and 2 parts of concentrated sulphuric acid for several hours to 125° under low pressure. This body was first introduced into commerce under the name Yara-yara, although the Yara-yara of commerce is now described as having an acacia odour. The corresponding ethyl ether $C_{10}H_7OC_2H_5$ melts at 37°, and has been introduced into commerce under the name "Bromelia". In some price-lists nerolin and Bromelia are given as synonyms. Its odour is not quite describable, and is incorrectly referred to that of pine-apples in older literature.

Synthetic neroli oil, being a mixture of various bodies (see *neroli oil*) is naturally much more variable in composition. Whilst the well-known alcohols geraniol and linalol, together with their acetic esters, enter into the composition of the oil, its characteristic odour is certainly due to other bodies; of these the best defined, the discovery

of which was first announced by E. & H. Erdmann (*Berichte*, 1899, p. 1213), is the methyl ester of anthranilic acid. This body is a crystalline solid, melting at 25° to a liquid oil, with a fine blue fluorescence, of specific gravity 1·168 at 15°, and boiling at 132° under a pressure of 14 mm. Its constitution is—



Anthranilic acid (*ortho*-amidobenzoic acid) was first prepared from indigo, but is now manufactured by reducing *ortho*-nitrobenzoic acid with tin and hydrochloric acid, or by oxidising aceto-*ortho*-toluidine with potassium permanganate, and boiling the resulting product with hydrochloric acid. The pure acid forms long needles melting at 144°. It is converted into its methyl ester by means of condensation with pure methyl alcohol in the presence of acids.

The artificial neroli oils of commerce are very uneven in value, as their composition is by no means constant. Although the exact composition is kept a trade secret, any practical perfumer can easily make an artificial neroli oil to closely imitate the pure natural oil, by experimental mixtures of geraniol, linalol and their acetic esters, and anthranilic methyl ester and β-naphtol methyl ether.

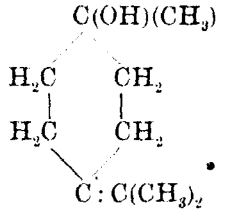
Artificial Lilac.—The well-known body, terpineol $C_{10}H_{17}OH$, possesses an odour which, especially when the substance is diluted, more closely resembles lilac than any other flower. At the same time it recalls elder flowers and hyacinth, and is consequently used with other bodies as the basis of many artificial perfumes. It may here be advisable

to emphasise that the practical perfumer should employ pure terpineol as the basis of his floral perfumes of this nature, as a little practice will soon enable him to reproduce the commercial products by the admixture of the proper quantity of other substances, often at half the cost of these products offered under fancy names. Muguet is a favourite perfume, of a more or less pronounced lilac odour (although the name is merely the French equivalent of lily of the valley). A mixture of terpineol (90 per cent.) with palmarosa oil (10 per cent.) will serve the purpose of this perfume in every respect. Syringol, or syringa oil, may be replaced by terpineol, if necessary with the addition of traces of various other oils. Lilacine and gardenia extract may be substituted by a mixture of terpineol and heliotropin (10 to 20 per cent.) with a trace of linalol or geraniol. In general lilac extracts, or "white lilac" may be regarded as solutions of terpineol, which are slightly modified by the addition of other perfumes, according to taste. For soap perfumery 1 per cent. of terpineol is sufficient, and the resulting soap is admirably perfumed. On account of its stability, neither heat, alkalies nor acids have any appreciable effect on this perfume, hence its utility in this branch of perfumery. For excellent results the following perfumes may be added. Oils of ylang-ylang, geranium, sandalwood or rose, or crystalline heliotropin. The latter body, however, does not stand the effects of heat.

Terpineol comes into commerce in two forms—the liquid and the crystalline, and although the latter is by far the more expensive, the former is of finer odour. Many commercial specimens have very poor odours and are by no means pure.

It appears more than probable that pure terpineol (see page 27) is a solid crystalline body, melting at 35° and boiling at 217°, at 760 mm. Its specific gravity at 20° in

the solid state is ·9057. The liquid terpineol of commerce is in all probability merely terpineol with traces of impurities which prevent its crystallising. It is a viscous liquid, of specific gravity ·940 to ·945, boiling at 215° to 218°. It is optically inactive, but Semmler has prepared it in both optically active varieties by replacing the chlorine in both of the limonene monohydrochlorides, by the hydroxyl group. Baeyer has synthesised an *isomeric* terpineol, of similar odour, which occurs in crystals melting at 69° to 70°, and which almost certainly has the constitution—



Possibly ordinary liquid terpineol consists of a mixture of this terpineol and that of melting point 35°, with traces of impurities.

The ordinary method of preparing terpineol is from terpin-hydrate $C_{10}H_{20}O_2 + H_2O$. This body is prepared by (*for example*) the following process, described by Hempel (*Ann. Chem.*, xxx., p. 71): "Eight parts of oil of turpentine are mixed with two parts of alcohol and two parts of nitric acid (specific gravity = 1·25) in a flat basin. After a few days the liquid is poured off from the crystals which have already separated, and is neutralised with an alkali, after which another crop of crystals separates. The preparation only succeeds during cool weather, as in summer a resinous mass is usually obtained." Terpin-hydrate forms large, transparent monosymmetric prisms melting at 117°. From this body Wiggers obtained by the action of hydriodic acid a compound which was investigated by List, and named by

him *terpinol*. It was described as a colourless oil with a pleasant odour of hyacinths. Tilden (*Jour. Chem. Soc.*, xxxiii., p. 247, and xxxv., p. 287) showed that this was a mixture of at least one terpene with an oxygenated body, and Wallach (*Annalen*, ccxxx., p. 251) showed that it was a mixture of the terpenes dipentene, terpinene and terpinolene with the oxygenated body terpineol $C_{10}H_{17}OH$.

There is on the market also a body called terpinolene, which is not the pure terpene of this name, but a mixture of the terpenes obtained when manufacturing terpineol, and which is offered as a cheap lilac perfume. It can scarcely be recommended, however, as its odour is very weak.

Terpineol is prepared in various ways. According to Voiry and Bouchardat, terpin-hydrate is heated with very dilute sulphuric acid (1 per cent.), and the resulting terpineol is purified by crystallisation and fractionation. Wallach (*Annalen*, ccxxx., p. 264) recommends treating twenty-five parts of terpin-hydrate with fifty parts of phosphoric acid (specific gravity = 1·12). The resulting product is steam-distilled and fractionated. Flawitzky (*Berichte*, xii., p. 2354) recommends allowing one part of French turpentine oil to stand for twelve hours, with half its weight of concentrated sulphuric acid and one and a half times its weight of 90 per cent. alcohol. Renard recommends the electrolysis of a mixture of alcohol, turpentine and sulphuric acid. Bertram and Walbaum have patented the following method (German patent, 67,255). Two kilogrammes of acetic acid are mixed with 50 grammes of sulphuric acid and 50 grammes of water. Into the mixture, heated to boiling, 1 kilogramme of rectified turpentine oil is poured, in portions of 200 grammes at a time. After cooling and standing the liquid is diluted with water and shaken with soda solution. The product consists of terpinene and terpineol esters, which are separated

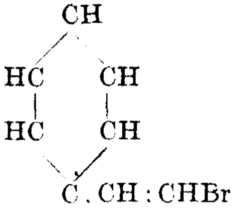
by fractional distillation. The esters, on treatment with alcoholic potash, yield terpineol.

Ertschikowsky's process consists of allowing 450 grammes of pinene to stand for a day with 900 grammes of acetic acid and 100 grammes of zinc chloride. The reaction product contains several bodies, amongst which is terpineol acetate, which on saponification yields solid terpineol.

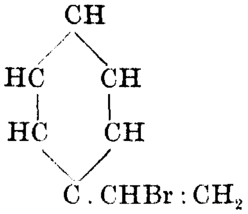
In order to keep this perfume at its best it should be stored in well-corked, dark-coloured bottles.

Artificial Hyacinth.—Several artificial hyacinth oils are on the market which are fairly good imitations of the natural perfume. As has been already mentioned, terpineol has a certain resemblance, although not a very close one, to this perfume, hence it forms an ingredient in most of the commercial "hyacinth extracts," etc. The artificial oils, however, contain several bodies of powerful odour, but their exact composition is kept as a trade secret, and their analyses have not been published. The following bodies, however, in addition to terpineol, have odours recalling hyacinths, and doubtless enter into the composition of the artificial oils:—

a-Chlorstyrolene and *a*-bromstyrolene are both oils of characteristic hyacinth odour. Styrolene or phenyl-ethylene $C_6H_5 . CH : CH_2$ is a hydrocarbon occurring in storax, but it can easily be produced by several synthetic reactions, such as by the action of alcoholic potash on bromethyl benzene, $C_6H_5 . CH_2 . CH_2Br$. It is best obtained by acting with soda solution on *β*-bromhydrocinnamic acid. It is a mobile, strongly refracting liquid of agreeable odour. It is optically inactive, boils at 144°, and has a specific gravity ·925 at 0°. It yields two series of derivatives in which the hydrogen of the side chain suffers replacement. For example, the bromine derivatives have the constitutions—



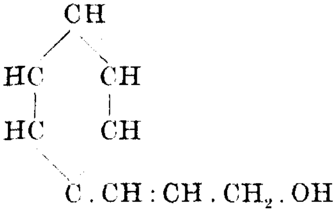
α-bromstyrolene.



β-bromstyrolene.

It is remarkable that the β-bromine and chlorine derivatives are oils which have a penetrating odour, producing a copious flow of tears; the α derivatives are oils with a sweet, hyacinth-like odour. α-Chlorstyrolene boils at 199°, and α-bromstyrolene melts at 7° and boils at 220°.

Styryl alcohol $C_9H_{10}O$, also known as cinnamyl alcohol or cinnyl alcohol or styrone, has a powerful odour, recalling hyacinths. It has the constitution—



and is obtained by saponifying its cinnamic ester, styracine, which occurs in storax and balsam of Peru. It forms shining needles, melting at 33° and boiling at 250°.

Benzyl alcohol $C_6H_5 . CH_2 . OH$ is an aromatic body in which the odour of bitter almonds and hyacinths may be traced. It is easily produced by various reactions, amongst which is the action of water on benzyl chloride. The latter body is obtained by the action of chlorine on boiling toluene, and is converted into benzyl alcohol by boiling with water and lead hydroxide, or even with water alone:—

$$C_6H_5CH_2Cl + H_2O = C_6H_5CH_2OH + HCl.$$

Pure benzyl alcohol is a liquid of specific gravity 1·0628 at 0°, or 1·0507 at 15°, and boils at 206°.

Artificial hyacinth oil no doubt contains some or all of these bodies with possibly some aromatic esters in addition. The author, however, has not analysed this substance.

Artificial Lemon Oil.—There are on the market preparations which bear the label "synthetic oil of lemon (terpeneless)" and which possess a strong lemon odour. The term synthetic is, in the author's opinion, quite unjustifiable, as samples he has examined consist chiefly of lemon-grass citral, which is not a synthetic product. Citral in a diluted form has been strongly recommended as a substitute for lemon oil by Messrs. Schimmel & Co., who in their report for October, 1896, say "normal lemon oil contains on the average about 7·5 per cent. of citral. Therefore 75 grammes of citral would suffice as a substitute for 1 kilo of oil of lemon. But its flavour is somewhat wanting in the degree of freshness characteristic of good lemon oil; but this slight deficiency is fully neutralised by an addition of lemon oil. Therefore citral is now generally used in combination with oil of lemon. The most approved proportion is 100 grammes of citral to 1400 grammes of oil of lemon. This is equivalent in odoriferous strength to 3 kilogrammes of oil of lemon.

"Fifteen grammes of the mixture are sufficient for making 1 hectolitre of lemon liquor, and this remains clear even if it contains only 30 per cent. of alcohol. For making lemon syrup to be used for lemonades, 20 to 25 grammes are sufficient for 100 kilos of syrup. When the use of citral is preferred without the addition of oil of lemon, the following solution deserves the preference: 75 grammes of citral and 925 grammes of alcohol (95 per cent.). This equals 1 kilogramme of oil of lemon in odoriferous power."

This statement is in the author's opinion quite incorrect. Citral is in no sense a substitute for oil of lemon. Not only

does it lack the fine aroma which the presence of aromatic esters such as geranyl acetate, and other as yet unidentified bodies give to true lemon oil, but it is very difficult to remove from it the last traces of the lemon-grass odour and taste, which by no means improve it for the purpose for which it is recommended. Further, the fact that the solution of citral in alcohol is admitted to lack the characteristic lemon freshness, makes it exceedingly illogical to say that the deficiency is neutralised by adding true lemon oil. What actually happens is that the true lemon oil covers the poor odour of the artificial mixture, but merely gives to the whole the average value of the ingredients. Users of lemon oil should not be deceived, however, by the term "synthetic oil of lemons". If a cheap substitute is wanted it should be bought under the name of citral, and the individual user must then decide for himself whether it suits his purpose.

Artificial Rose Oil.—Although numerous "artificial" and "synthetic" rose oils are listed by various firms, there is nothing which in any way competes with the fine odour of natural otto of roses. These artificial ottos or oils of roses are, as a rule, merely clumsy imitations of the natural product. The absurdity of some of them is accentuated when they not only imitate the true oil in odour but also in appearance, for the crystalline stearoptene of natural oil of roses is quite odourless, but yet some "artificial" oils are made to solidify at the same temperature as the genuine oil. Indeed in most cases artificial oils of roses may be described as quite unscientific attempts at artificial perfumery. The two best defined constituents of oil of roses are the alcohols geraniol and citronellol, and these bodies with a trace of their acetic esters will produce as good an "artificial oil of roses" as may be. A little genuine oil of roses is frequently added to make the substitute a little more passable. The chemistry of geraniol and citronellol have already been dealt with at some length,

but the following details of the practical methods of their preparation will not be out of place in the present chapter.

Geraniol $C_{10}H_{17}OH$ (see page 34) has been the subject of several patents. Amongst these may be classed that for the preparation of "rhodinol" from geranium and pelargonium oil (German patent 80,007). To prepare rhodinol the oil is distilled under reduced pressure (14 mm.), and the fraction 120° to 130°, consisting of impure rhodinol, is heated in an autoclave with acetic anhydride, and the resulting esters are fractionated. The fraction 127° to 132°, consisting of the acetic ester of "rhodinol," is saponified with alkali, and the resulting oil is fractionated *in vacuo*. The portion distilling between 120° and 125° is an oily colourless fluid with a rose-like odour, and is the commercial rhodinol.

A patent was taken out for the preparation of geraniol from citronella oil by Schimmel & Co. (German patent 76,435). Here either the citronellic aldehyde is removed by means of alkaline bisulphite or polymerised by alkalies, and the geraniol obtained by fractional distillation.

Jacobsen's method, which is adopted for the purification of geraniol, depends on the fact that geraniol yields a crystalline compound with calcium chloride. The geraniol containing fractions of the oil are well rubbed with freshly fused calcium chloride and the mixture allowed to stand *in vacuo* at a low temperature. The compound $2C_{10}H_{18}O \cdot CaCl_2$ crystallises out and is washed with absolute ether and decomposed with water, when pure geraniol is set free. The geraniols of commerce vary very much in odour (and therefore in purity), but the best varieties do not possess anything like so fine an odour as rose oil. It is customary, too, to distil geraniol over various flowers, such as roses, mignonette, or hyacinths, and sell the resulting perfume as rose-geraniol, mignonette-geraniol, etc. These perfumes are of much more delicate and finer odours than ordinary geraniol.

Citronellol occurs associated with geraniol, and unless removed specially, always occur in the alcoholic bodies separated from the various geranium oils. The compounds described under the names of rhodinol, réuniol and roseol appear to be mixtures of both alcohols.

Mentho-citronellol (*q. v.*) $C_{10}H_{19}OH$, prepared by Wallach (*Ann. Chem.*, cclxxviii., p. 302, and ccxcvi., p. 129), is possibly identical, possibly isomeric with citronellol. It has a strong rose odour. A body patented by Schering (German patent 96,657), and which is described under the name *di-methyl-heptadineol*, also possesses a strong rose odour. This body, which possesses the formula $C_9H_{16}O$, has a fair rose odour. It is prepared by a series of very complex reactions, but as the body has not much practical interest the reader is referred to the original patent for the details.

Niobe Oil.—The synthetic perfume sold under this name is merely methyl benzoate $C_6H_5 . COOCH_3$. It is a liquid of specific gravity 1·103 at 15°, and boils at 195° to 196°. It can be prepared by dissolving benzoic acid in excess of methyl alcohol CH_3OH, and saturating the solution with dry hydrochloric acid gas. The whole is warmed to 100° for a few hours, and then water is added, which throws out the oil which is purified by rectification.

Bergamiol.—This body, which is used as a substitute for bergamot oil, and which it resembles very fairly, is simply linalyl acetate $C_{10}H_{17} . C_2H_3O_2$ (*q. v.*). It is prepared by heating linalol with the calculated quantity of acetic anhydride for a few hours and distilling the resulting oil under reduced pressure after being washed with weak alkali. It is purified by rectification *in vacuo*.

Artificial Jasmin Oil.—The natural jasmin perfume is due to an essential oil (*q. v.*), but as this is both exceedingly delicate and expensive, it is generally extracted in the form of a pomade. There are, however, several brands of syn-

thetic oil of jasmin on the market, the exact composition of which is kept secret. None of them are single compounds, but are mixtures of several odoriferous bodies which together reproduce the jasmin perfume very fairly. According to Verley (*Comptes Rendus*, 30th Jan., 1899), the natural oil consists of about 10 per cent. of linalol and 90 per cent. of phenyl-glycol-methylene acetal. These results led to the taking out of a French patent for artificial oil of jasmin. Hesse and Müller deny the existence of the latter body in jasmin oil, or that it has a jasmin odour. They claim that benzyl acetate is the chief constituent of the oil, and they state that the average composition of the oil is as follows: benzyl acetate, 65 per cent.; linalyl acetate, 7·5 per cent.; benzyl alcohol, 6 per cent.; linalol, 16 per cent. About 5 per cent. of other odorous bodies occur, the nature of which is not given. As previously stated, secondary styrolyl acetate $C_6H_5.CH(O.COCH_3)CH_3$ has a marked jasmin odour. Artificial jasmin oil is made on the basis of these researches, although probably small quantities of some bodies not generally known are added by the manufacturers. The chemistry of benzyl alcohol, linalol and linalyl acetate have already been referred to in detail. Benzyl acetate is a liquid of specific gravity 1·057, prepared by acetylating the alcohol. Its boiling point is 206°. Secondary styrolene acetate is an oil boiling at 217° to 220° prepared in the following manner. Ethyl-benzene $C_6H_5.C_2H_5$ is prepared by heating benzene with aluminium chloride and ethyl bromide. By acting on this body with bromine at the boiling temperature of the liquid, β-brom-ethyl-benzene $C_6H_5.CHBr.CH_3$ is formed, which by the action of silver acetate and acetic acid is converted into secondary styrolyl acetate $C_6H_5.CH(O.COCH_3)CH_3$.

Artificial Cognac Oil.—Cognac oil, which is perhaps not an essential oil in the fullest sense, is prepared by distilling

wine lees with seven or eight times their weight of water. It is the commercial "œnanthic ether," but is in reality a mixture of various ethers of several of the higher fatty acids, and is used for flavouring poor quality brandies made from corn, spirit, etc., and for flavouring various liqueurs, etc. The artificial oil is easily made from the ethyl ethers of œnanthylic, caprylic and capric acids. Œnanthylic ether $CH_3(CH_2)_5 . CO_2C_2H_5$ is a liquid boiling at 188°. Caprylic ether $CH_3(CH_2)_6CO_2 . C_2H_5$ boils at 207° to 208°, and capric ether $CH_3(CH_2)_8 . CO_2C_2H_5$ boils with decomposition between 240° and 245°. The ethers prepared from the fatty acids of cocoanut oil, which include caprylic, caproic, capric, lauric, myristic and palmitic acids, are used as a basis for cognac essence.

The researches of Ordonneau (*Comptes Rendus*, cii., p. 217) are of great importance, as they embrace an exhaustive examination of a sample of cognac twenty-five years old of very fine quality. He was able to identify the following bodies in this brandy, and from these results an excellent artificial cognac oil can be made, with modifications to suit individual tastes. He found in each 100 litres :—

Acetic aldehyde . .	3 grammes.	Amine bases . .	4 grammes.
Acetal . . .	35 ,,	Ethyl acetate . .	35 ,,
Butyl alcohol . .	218·6 ,,	Propyl alcohol . .	40 ,,
Hexyl alcohol . .	1·5 ,,	Amyl alcohol . .	83·6 ,,
Propionic, butyric and caproic ethers .	3 ,,	Œnanthic ether . .	4 ,,

At the same time, it must be remembered that these results are exceptional, and the ordinary cognac oil is chiefly composed of ethers, the most important being œnanthic ether.

Artificial oils of almond (benzaldehyde and nitrobenzene), cassia (cinnamic aldehyde), wintergreen (methyl salicylate), garlic (allyl sulphide), and mustard (allyl isothiocyanate) have already been described under their respective oils.

These are all chemical individuals, and may be called true synthetic oils, and in this respect differ from many of the above-mentioned "artificial oils". The former are definite bodies of definite characteristics, whereas the latter are mixtures of several odorous constituents, which vary in proportions in the different brands on the market, and with a supply of the more common aromatic alcohols, esters and other bodies, the intelligent perfumer can reproduce very fairly many of the natural perfumes. At the same time it should be remembered that it is an almost general rule that the artificial perfumes have usually a harsher and less delicate odour than the natural ones, and in some cases are only very poor substitutes. In certain cases, however, this is not so, and an almost unlimited field of research exists in the chemistry of perfumes with a view to their synthetic production. Regard, however, should be paid, not only to the main odorous constituent of a given perfume, but also to the traces of other bodies which exist, and which modify the odour to that extent which determines the difference between the artificial and the natural perfume. When more attention is paid to this point, the artificial product will more closely resemble the natural body. As examples, one may quote *pure* benzaldehyde and *pure* cinnamic aldehyde. These cannot be mistaken by an expert nose for natural oils of almond and cassia respectively. Some traces of other odorous bodies are missing, and to such traces of bodies existing in essential oils great attention should be paid.

APPENDIX.

TABLE OF CONSTANTS

OF THE

MORE IMPORTANT ESSENTIAL OILS.

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TABLE OF CONSTANTS OF THE MORE IMPORTANT ESSENTIAL OILS.

Specific gravities are given for 15·5° C. and optical rotations for a column of 100 mm., unless otherwise stated.

Note.—The most important constituents are printed in heavier type than the remainder.

Oil.	Source.	Yield Per Cent.	Specific Gravity.	Optical Rotation.	Constituents.
Ajowan oil	Ptychotis ajowan; fruit	3·0-4·0	·900-·930	dextro-rotary	**Thymol** $C_{10}H_{14}O$; cymene $C_{10}H_{14}$; terpene.
Almond oil (bitter)	Amygdalus communis; fruit	·5-1·0	1·045-1·070	Inactive	**Benzaldehyde** C_6H_5COH; prussic acid HCN.
Ammoniacum oil	Dorema ammoniacum; resin	0·3	·890	dextro-rotary	
Angelica oil	Angelica officinalis; root	·25-1·0	·860-·905	+18° to +30°	Phellandrene $C_{10}H_{16}$; methyl-ethyl-acetic acid: oxypentadecylic acid.
Angostura oil	Galipea cusparia; bark	1·5	·930-·960	−36°	**Galipol** $C_{15}H_{26}O$; cadinene $C_{15}H_{24}$; galipene $C_{15}H_{24}$.
Aniseed oil	Pimpinella anisum; fruit	1·5-6·0	·980-990	0° to −2°	**Anethol** $C_{10}H_{12}O$; methyl chavicol $C_{10}H_{12}O$; anisic aldehyde $C_8H_8O_2$; anisic acid; anise ketone $C_{10}H_{12}O_2$ (?).
Aniseed oil (star)	Illicium verum; fruit	5·0	·980-990	0° to −2°	**Anethol** $C_{10}H_{12}O$; methyl chavicol $C_{10}H_{12}O$; anise aldehyde; anisic acid; ethyl hydroquinone; safrol; pinene $C_{10}H_{16}$; phellandrene $C_{10}H_{16}$.
Arnica oil	Arnica montana; root	1·0	·990-1·000	−1° to −2°	Phlorone isobutyric ether $C_{16}H_{26}O_2$; thymohydroquinone dimethyl ether $C_{12}H_{18}O_2$; phlorone dimethyl ether $C_{10}H_{14}O_2$; esters; hydrocarbons.
Asafœtida oil	Ferula species; resin	3·0-4·0	·975-·990	−10°	$C_7H_{14}S_2$; $C_{10}H_{20}S_2$; $C_8H_{16}S_2$; $C_{10}H_{18}S_2$; $C_{10}H_{16}O$; terpenes; sesquiterpene.
Asarum oil	Asarum Europæum; root	1·0	1·050-1·070	—	Asarone $C_{12}H_{16}O_3$; pinene $C_{10}H_{16}$; methyl eugenol $C_{11}H_{14}O_2$.

Asarum oil	Asarum Canadense; root . .	3·0-5·0	·930-·960	—	Terpene; asarone $C_{12}H_{16}O_3$; esters; methyl eugenol $C_{11}H_{14}O_2$.
Bay oil	Pimenta acris; leaves . .	2·0-3·0	·965-·995	− 0° 30′ to − 2°	**Eugenol** $C_{10}H_{12}O_2$; pinene $C_{10}H_{16}$(?); dipentene $C_{10}H_{16}$; methyl eugenol $C_{11}H_{14}O_2$; phellandrene $C_{10}H_{16}$; hydrocarbon $C_{10}H_{16}$; chavicol $C_9H_{10}O$; methyl chavicol $C_{10}H_{12}O$; citral $C_{10}H_{16}O$.
Bay oil (Californian) . .	Laurus Californica; leaves .	4·0	·930-·950	—	Cineol $C_{10}H_{18}O$; terpineol $C_{10}H_{18}O$ (?).
Bergamot oil . . .	Citrus bergamia; fruit . .	—	·882-·886	+ 8° to + 20°	Limonene $C_{10}H_{16}$; linalol $C_{10}H_{18}O$; **linalyl acetate** $C_{12}H_{20}O_2$; bergaptene $C_{12}H_8O_4$.
Betel oil	Piper betle; leaves . . .	·5-1·0	·958-1·045	+ 2° 50′	**Methoxy-chavicol** $C_{10}H_{12}O_2$; cadinene $C_{15}H_{24}$; chavicol $C_9H_{10}O$.
Buchu oil	Barosma species . . .	1·0-2·0	·940-·945	—	Diosphenol $C_{10}H_{16}O_2$; ketone $C_{10}H_{18}O$; hydrocarbon $C_{10}H_{18}$.
Cajuput oil . . .	Melaleuca species; leaves .	—	·920-·930	0° to − 2°	**Cineol** $C_{10}H_{18}O$; terpineol $C_{10}H_{18}O$; terpinyl esters; butyric, valeric and benzoic aldehydes; pinene $C_{10}H_{16}$ (?).
Calamus oil . . .	Acorus calamus; rhizome .	·8-5·0	·960-1·000	+ 12° to + 35°	Terpenes; sesquiterpene; oxygenated bodies not identified.
Camphor oil . . .	Camphora officinalis; wood and root	4·0	—	—	**Camphor** $C_{10}H_{16}O$; **safrol** $C_{10}H_{10}O_2$; pinene $C_{10}H_{16}$; phellandrene $C_{10}H_{16}$; cineol $C_{10}H_{18}O$; eugenol $C_{10}H_{12}O_2$; cadinene $C_{15}H_{24}$.
Caparrapi oil . . .	Nectandra caparrapi . .	—	·915-·935	− 3°	Caparrapiol $C_{15}H_{26}O$; an acid $C_{15}H_{24}O_3$.
Caraway oil . . .	Carum carui; seed . . .	3·0-7·0	·905-·920	+ 70° to + 85°	**Carvone** $C_{10}H_{14}O$; limonene $C_{10}H_{16}$.
Cardamom oil . . .	Elettaria cardamomum; fruit .	1·0-3·0	·936-·946	+ 34° to + 47°	Cineol $C_{10}H_{18}O$; terpineol $C_{10}H_{18}O$; acetic esters; limonene $C_{10}H_{16}$; dipentene $C_{10}H_{16}$.
Cardamom oil (Bengal) .	Amomum aromaticum; fruit .	1·12	·920	− 12° 41′	
Cardamom oil (Kameroon)	Amomum danielli; fruit . .	2·3	·907	− 20° 34′	
Cardamom oil (Siam) .	Amomum cardamomum; fruit	2·4	·905	+ 38° 4′	Borneol $C_{10}H_{18}O$; camphor $C_{10}H_{16}O$; **bornyl esters.**
Carrot oil	Daucus carota; seed . .	1·0-1·5	·870-·930	− 13° to − 40°	Pinene $C_{10}H_{16}$; terpineol $C_{10}H_{18}O$; cineol $C_{10}H_{18}O$.
Cascarilla oil . . .	Croton eleutheria; bark . .	1·0-3·0	·890-·930	+ 5°	Terpenes.
Cassia oil	Cinnamomum cassia . .	·5-2·0	1·050-1·065	+ 1° to − 1°	**Cinnamic aldehyde** C_9H_8O; terpenes; cinnamic esters; o-methyl-coumaric aldehyde $C_{10}H_{10}O_2$.

Oil.	Source.	Yield Per Cent.	Specific Gravity.	Optical Rotation.	Constituents.
Cedar oil	Juniperus virginiana ; wood	2·5-5·0	·940-·960	-25° to -40°	**Cedrene** $C_{15}H_{24}$; cedrol $C_{15}H_{26}O$.
Cedar leaf oil	Juniperus virginiana ; leaves	—	·883-·888	+55° to +65°	Limonene $C_{10}H_{16}$; cadinene $C_{15}H_{24}$; borneol $C_{10}H_{18}O$, and bornyl esters.
Celery oil	Apium graveolens ; seed	3·0	·870-·895	+65° to +80°	Limonene $C_{10}H_{16}$; sedanolic acid $C_{12}H_{20}O_3$; **sedanolide** $C_{12}H_{18}O_2$; sedanonic acid $C_{12}H_{18}O$; sesquiterpene ; guaiacol ; palmitic acid.
Chamomile oil (Roman)	Anthemis nobilis ; flowers	·5-1·0	·905-·915	—	Esters of tiglic and angelic acids $C_5H_8O_2$ (chiefly amyl and hexyl) ; isobutyl isobutyrate $C_8H_{16}O_2$, esters of an alcohol, anthemol $C_{10}H_{16}O$.
Chamomile oil (German)	Matricaria chamomilla ; flowers	.1-·3	·930-·940	—	Esters of caproic acid $C_6H_{12}O_2$; hydrocarbons.
Cheken-leaf oil	—	1·0	·880	+20°	Pinene $C_{10}H_{16}$; **cineol** $C_{10}H_{18}O$.
Chenopodium oil	Artemisia absinthium ; fruit	1·0	·900-·975	-5° to -18°	
Cherry-bark oil (wild)	Prunus virginiana ; bark	·2	1·050	Inactive.	**Benzaldehyde** C_6H_5COH ; prussic acid HCN.
Cherry-laurel oil	Prunus laurocerasus ; leaves	·5	1·050-1·065	Inactive.	**Benzaldehyde** C_6H_5COH ; prussic acid HCN.
Cinnamon oil	Cinnamomum zeylanicum ; bark	·5-1·0	1·025-1·035	0° to -1°	**Cinnamic aldehyde** C_9H_8O ; phellandrene $C_{10}H_{16}$; eugenol $C_{10}H_{12}O_2$.
Cinnamon-leaf oil	Cinnamomum zeylanicum ; leaves	1·5-2·0	1·045-1·060	-1° to +1°	**Eugenol** $C_{10}H_{12}O_2$; cinnamic aldehyde, C_9H_8O ; safrol $C_{10}H_{10}O_2$.
Citronella oil	Andropogon nardus ; grass	—	·885-·920	-4° to -16°	**Citronellal** $C_{10}H_{18}O$; geraniol $C_{10}H_{18}O$; borneol $C_{10}H_{18}O$; methyl-heptenone $C_8H_{14}O$; camphene $C_{10}H_{16}$; dipentene $C_{10}H_{16}$.
Citron oil	Citrus medica ; peel of fruit	—	·860-·870	+66° to +76°	Limonene $C_{10}H_{16}$; citral $C_{10}H_{16}O$.
Clove oil	Eugenia caryophyllata ; buds	14·0-19·0	1·049-1·065	0° to -1° 30′	**Eugenol** $C_{10}H_{12}O_2$; caryophyllene $C_{15}H_{24}$; amyl methyl ketone $C_7H_{14}O$; methyl alcohol, CH_4O ; furfurol $C_5H_4O_2$; aceteugenol (?).
Coriander oil	Coriandrum sativum ; seed	·2-1·0	·870-·885	+7° to +14°	**Linalol** $C_{10}H_{18}O$; pinene $C_{10}H_{16}$.
Costus oil	Aplotaxis lappa ; root	1	·980-·987	+15° to +16°	

Cubeb oil	Piper cubeba; fruit	10·0-18·0	·910-·930	−30° to −40°	Cadinene $C_{15}H_{24}$; dipentene $C_{10}H_{16}$; cubeb camphor $C_{15}H_{26}O$.
Culilaban oil	Cinnamomum culilavan; fruit	3·0-4·0	1·050	—	Eugenol $C_{10}H_{12}O_2$; methyl-eugenol, $C_{11}H_{14}O_2$.
Cumin oil	Cuminum cyminum; fruit	2·5-4·0	·890-·930	+4° to +6°	Cymene $C_{10}H_{14}$; **cumic aldehyde** $C_{10}H_{12}O$.
Dill oil	Anethum graveolens; fruit	3·0-4·0	·900-·920	+70° to +80°	**Carvone** $C_{10}H_{14}O$; limonene $C_{10}H_{16}$; a paraffin hydrocarbon.
Dill oil (East Indian)	Anethum Sowa; fruit	2·0-3·0	·970	+40°	Carvone $C_{10}H_{14}O$; limonene $C_{10}H_{16}$; dill apiol $C_{12}H_{14}O_4$.
Dog-fennel oil	Eupatorium foeniculaceum; herb	—	·935	+18°	Phellandrene $C_{10}H_{16}$.
Elecampene oil	Inula helenium; root	1·0-2·0	—	—	Alantic acid $(C_6H_8O)_x$; alanto-lactone, alantol.
Eucalyptus oils; leaves—					
,, **Amygdalina**	—	To 4·0	·855-·890	−25° to −80°	**Phellandrene** $C_{10}H_{16}$; cineol $C_{10}H_{18}O$.
,, **Backhousia**	—	To 4·0	·895-·902	—	**Citral** $C_{10}H_{16}O$; phellandrene $C_{10}H_{16}$.
,, **Baileyana**	—	1·0	·890-·920	—	**Cineol** $C_{10}H_{18}O$; citral $C_{10}H_{16}O$; phellandrene $C_{10}H_{16}$.
,, **Capitellata**	—	—	·915	—	**Cineol** $C_{10}H_{18}O$; eudesmol.
,, **Cneorifolia**	—	—	·915-·925	−5° to +5°	**Cineol** $C_{10}H_{18}O$; cumic aldehyde $C_{10}H_{12}O$.
,, **Corymbosa**	—	4·0	·880	—	Citral $C_{10}H_{16}O$ (?); geraniol $C_{10}H_{18}O$ (?); cineol $C_{10}H_{18}O$.
,, **Crebra**	—	—	—	—	**Cineol** $C_{10}H_{18}O$.
,, **Dealbata**	—	3·0	·885-·900	—	**Citronellal** $C_{10}H_{18}O$; citronellol $C_{10}H_{20}O$; geraniol $C_{10}H_{18}O$ (?); citral $C_{10}H_{16}O$ (?);
,, **Dextro-pinea**	—	0·8	·873-·876	dextro-rotary	**Dextro-pinene** $C_{10}H_{16}$; aldehydes.
,, **Dumosa**	—	—	·900-·912	—	**Cineol** $C_{10}H_{18}O$.
,, **Eugenoides**	—	0·7	·905-·910	+4° to +6°	**Cineol** $C_{10}H_{18}O$; phellandrene $C_{10}H_{16}$.
,, **Globulus**	—	0·8-1·5	·910-·930	+1° to +10°	**Cineol** $C_{10}H_{18}O$; pinene $C_{10}H_{16}$; ethyl alcohol C_2H_6O; amyl alcohol $C_5H_{12}O$; butyric, caproic and valeric aldehydes.
,, **Goniocalyx**	—	—	·915-·920	—	Cineol $C_{10}H_{18}O$.
,, **Gracilis**	—	—	—	—	Cineol $C_{10}H_{18}O$.
,, **Hæmostoma**	—	2·0	·880-·890	—	Cymene $C_{10}H_{14}$; **cumic aldehyde** $C_{10}H_{12}O$.
,, **Incrassata**	—	—	—	—	Cineol $C_{10}H_{18}O$.
,, **Laevo-pinea**	—	0·7	·873	laevo-rotary	**Laevo-pinene** $C_{10}H_{16}$.
,, **Leucoxylon**	—	1·1	·920-·925	—	**Cineol** $C_{10}H_{18}O$.

Oil.	Source.	Yield Per Cent.	Specific Gravity.	Optical Rotation.	Constituents.
Eucalyptus oils; leaves—					
„ **Loxophleba**	—	—	·883	+5°	Cineol $C_{10}H_{18}O$; phellandrene $C_{10}H_{16}$; aldehydes.
„ **Macrorhyncha**	—	0·3	·927	—	**Cineol** $C_{10}H_{18}O$; phellandrene, $C_{10}H_{16}$; esters; eudesmol.
„ **Maculata var. Citriodora**	—	1·0-4·0	·870-·905	·0° to +2°	**Citronellal** $C_{10}H_{18}O$; geraniol $C_{10}H_{18}O$.
„ **Microcorys**	—	1·0-2·0	·895-·930	—	**Cineol** $C_{10}H_{18}O$.
„ **Obliqua**	—	—	·895-·915	−7°	**Cineol** $C_{10}H_{18}O$; phellandrene $C_{10}H_{16}$.
„ **Odorata**	—	1·5	·900-·925	—	**Cineol** $C_{10}H_{18}O$; phellandrene $C_{10}H_{16}$; cumic aldehyde $C_{10}H_{12}O$.
„ **Oleosa**	—	1·3	·905-·930	−5° to +5°	**Cineol** $C_{10}H_{18}O$.
„ **Populifolia**	—	—	—	—	**Cineol** $C_{10}H_{18}O$; cumic aldehyde $C_{10}H_{12}O$.
„ **Punctata**	—	0·6-1·2	·912-·921	−3° to +5°	**Cineol** $C_{10}H_{18}O$.
„ **Planchoniana**	—	—	·915	—	Citronellal $C_{10}H_{18}O$.
„ **Resinifera**	—	—	·900	−15° to −20°	**Cineol** $C_{10}H_{18}O$.
„ **Rostrata**	—	—	·915-·930	−2° to +13°	**Cineol** $C_{10}H_{18}O$; valeric aldehyde $C_5H_{10}O$.
„ **Risdonia**	—	—	·910-·925	−2° to −6°	**Cineol** $C_{10}H_{18}O$; phellandrene $C_{10}H_{16}$.
„ **Staigeriana**	—	—	·880	—	**Citral** $C_{10}H_{16}O$.
Fennel oil	Foeniculum vulgare; fruit	1·0-6·0	·960-·980	+6° to +20°	Pinene $C_{10}H_{16}$; phellandrene $C_{10}H_{16}$; dipentene $C_{10}H_{16}$; limonene $C_{10}H_{16}$; fenchone $C_{10}H_{16}O$; **anethol** $C_{10}H_{12}O$.
Feverfew oil	Pyrethrum parthenium; flowers	·1-·4	·900-·960	—	Borneol $C_{10}H_{18}O$ and its esters.
Fir cone oil	Abies excelsa; cones	—	·855-·870	to −80°	Pinene $C_{10}H_{16}$; limonene $C_{10}H_{16}$; **bornyl acetate** $C_{12}H_{20}O_2$ (1 to 2 %).
Fleabane oil	Erigeron canadensis; herb	·5	·850-·890	+50°	Limonene $C_{10}H_{16}$; terpineol $C_{10}H_{18}O$.
Galangal oil	Alpinia galanga; rhizome	·5-1·5	·915-·925	−1° to −4°	Cineol $C_{10}H_{18}O$.
Galbanum oil	Peucedanum galbaniflurum; resin	12·0-24·0	·910-·940	−5° to +20°	Pinene $C_{10}H_{16}$; cadinene $C_{15}H_{24}$.
Garlic oil	Allium Sativum; herb	0·1	1·052	Inactive	Allyl-propyl-disulphide $C_6H_{12}S_2$; **diallyl disulphide** $C_6H_{10}S_2$; $C_6H_{10}S_3$; $C_6H_{10}S_4$.
Geranium oil	Pelargonium species; herb	—	·888-·905	−6° to −16°	**Geraniol** $C_{10}H_{18}O$; citronellol $C_{10}H_{20}O$ and tiglic acid esters.
Geranium oil (Indian)	Andropogon schoenanthus; grass	·3-·4	·885-·896	+2° to −2°	**Geraniol** $C_{10}H_{18}O$; geranyl esters; dipentene $C_{10}H_{16}$; *methyl-heptenone* $C_8H_{14}O$ (?)

Ginger oil	Zingiber officinale; rhizome	2·0-3·0	·872-·885	−25° to −45°	Phellandrene $C_{10}H_{16}$; camphene $C_{10}H_{16}$; sesquiterpene.
Golden-rod oil	Solidago canadensis, and other species	—	·859	−11° 10′	Terpenes: **borneol** $C_{10}H_{18}O$; **bornyl acetate** $C_{12}H_{20}O_2$; cadinene $C_{15}H_{24}$.
Grains of Paradise oil	Amomum Melegueta; seeds	·75	·894	−4°	
Hedychium oil	Hedychium coronarium; flowers	—	·869	−0° 28′	Pinene $C_{10}H_{16}$.
Helichrysum oil	Helichrysum stoechas; herb	—	·873	—	Terpenes and sesquiterpenes.
Hemp oil	Cannabis sativa; herb	·1	·930	−10° to −12°	Cannibene $C_{15}H_{24}$.
Hemp oil (Indian)	Cannabis Indica; herb	—	·930	—	
Heracleum oil	Heracleum sphondylium; fruit	1·0-3·0	·860-·880	dextro-rotary	Octyl alcohol $C_8H_{18}O$; octyl acetate $C_{10}H_{20}O_2$; octyl caproate $C_{14}H_{28}O_2$; ethyl butyrate $C_6H_{12}O_2$.
Hop oil	Humulus lupulus; flowers	·3-1·0	·855-·882	to +1°	Humulene $C_{15}H_{24}$; geraniol $C_{10}H_{18}O$; tetrahydrocymene $C_{10}H_{18}$ (?); terpenes.
Jasmin oil	Jasminum grandiflorum: flowers	traces only.	1·009-1·018	+2° 30′ to +3° 30′	**Benzyl acetate** $C_9H_{10}O_2$; linalyl acetate $C_{12}H_{20}O_2$; benzyl alcohol C_7H_8O; linalol $C_{10}H_{18}O$.
Juniper-berry oil	Juniperus communis; berries	·5-1·5	·865-·890	−4° to −7°	Cadinene $C_{15}H_{24}$; pinene $C_{10}H_{16}$; an alcohol, m. p. 165°, and its acetic ester.
Kaempferia oil	Kaempferia rotunda; root	·2	·945-·950	+12°	Cineol $C_{10}H_{18}O$.
Kiku oil	Pyrethrum Indicum; leaves	—	·880-·890	—	
Kuromoji oil	Lindera sericea; leaves and twigs	—	·890-·915	laevo-rotary	Limonene $C_{10}H_{16}$; dipentene $C_{10}H_{16}$; terpineol $C_{10}H_{18}O$; carvone $C_{10}H_{14}O$.
Laurel oil	Laurus nobilis; leaves	1·0-3·0	·920-·930	−15 to −18°	Pinene $C_{10}H_{16}$; cineol $C_{10}H_{18}O$.
Lavender oil	Lavandula vera; flowers	—	·885-·900	−5° to −10°	Linalyl acetate $C_{12}H_{20}O_2$ (English 7-10%; French 25-40%); pinene $C_{10}H_{16}$; limonene $C_{10}H_{16}$; geraniol $C_{10}H_{18}O$; sesquiterpene; cineol $C_{10}H_{18}O$ (in English oil).
Lemon oil	Citrus limonum; peel	—	·857-·862	+59° to +65°	**Citral** $C_{10}H_{16}O$; citronellal $C_{10}H_{18}O$; limonene $C_{10}H_{16}$; geranyl and linalyl acetates $C_{12}H_{20}O_2$; phellandrene $C_{10}H_{16}$; stearoptene.
Lemon-grass oil	Andropogon citratus; grass	—	·895-·905	+3° to −3°	**Citral** $C_{10}H_{16}O$; citronellal $C_{10}H_{18}O$; geraniol $C_{10}H_{18}O$; methyl heptenone $C_8H_{14}O$; esters and terpenes.
Lime oil	Citrus limetta; fruit	—	·870-·875	+56° to +60°	**Linalyl acetate** $C_{12}H_{20}O_2$; limonene $C_{10}H_{16}$; linalol $C_{10}H_{18}O$.

Oil.	Source.	Yield Per Cent.	Specific Gravity.	Optical Rotation.	Constituents.
Lime oil	Citrus medica var. acida (expressed)	—	·873-·885	+35° to +40°	Limonene $C_{10}H_{16}$; citral $C_{10}H_{16}O$; limettin $C_{11}H_{10}O_4$.
Lime oil	Citrus medica var. acida (distilled)	—	·856-·868	+40°	
Linaloe oil	Bursera species	7·0-12·0	·872-·895	-4° to -13°	**Linalol** $C_{10}H_{18}O$; geraniol $C_{10}H_{18}O$; methyl heptenone $C_8H_{14}O$.
Lovage oil	Levisticum officinale; roots	1·0	1·005-1·045	+2° to +7°	Terpineol $C_{10}H_{18}O$.
Mace oil	Myristica fragrans; arillus	4·0-15·0	·910-·932	+10°	Pinene $C_{10}H_{16}$; dipentene $C_{10}H_{16}$; myristicol $C_{10}H_{16}O$; myristicin $C_{12}H_{14}O_3$; a phenol.
Marjoram oil	Origanum majorana; herb	·3-1·0	·890-·910	+15° to +20°	
Marjoram oil (Cretic)	Origanum Smyrnaeum	—	·915-·945	-3° to -15°	**Carvacrol** $C_{10}H_{14}O$; linalol $C_{10}H_{18}O$; cymene $C_{10}H_{14}$.
Marsh tea oil	Ledum palustre; leaves	·5-1·0	·925-·935	—	**Ledum camphor** $C_{15}H_{26}O$.
Massoi bark oil	Massoia aromatica; bark	6·0-8·0	1·040-1·060	—	**Eugenol** $C_{10}H_{12}O_2$; safrol $C_{10}H_{10}O_2$; pinene $C_{10}H_{16}$; limonene $C_{10}H_{16}$.
Masterwort oil	Imperatoria ostruthium; root	1·0	·875	—	Angelic aldehyde (?) C_5H_8O.
Matico oil	Piper angustifolium; leaves	·5-3·5	·930-1·070	+5°	Asarone $C_{12}H_{16}O_3$; matico camphor $C_{12}H_{20}O$.
Meadowsweet oil	Spiræa ulmaria; herb	—	—	—	Salicylic aldehyde $C_7H_6O_2$; terpene.
Melissa oil	Melissa officinalis; herb	traces only	·890-·925	0° 30′ to -6° 30′	**Citral** $C_{10}H_{16}O$; citronellal $C_{10}H_{18}O$; geraniol $C_{10}H_{18}O$; linalol $C_{10}H_{18}O$; citronellol $C_{10}H_{20}O$.
Mew oil	Meum anthamanticum; root	0·75	1·001	—	
Mountain mint oil	Pycnanthemum incanum; herb	1·0	·910-·940	+3° to +5°	Carvacrol $C_{10}H_{14}O$; pulegone $C_{10}H_{16}O$.
Musk root oil (sumbul)	Ferula sumbul; root	0·2-0·4	·950-·965	—	
Mustard oil	Sinapis nigra; seeds	—	1·014-1·032	0° to -1°	**Allyl thiocyanate** C_3H_5CNS; carbon disulphide CS_2; cyanallyl.
Myrtle oil	Myrtus communis; leaves	—	·895-·920	+10° to +20°	Pinene $C_{10}H_{16}$; cineol $C_{10}H_{18}O$; dipentene $C_{10}H_{16}$ (?).
Myrtle oil (bog)	Myrica gale; leaves	1·0	·870	—	
Myrtle oil (wax)	Myrica cerifera; leaves	·02-·05	·885	-5°	
Neroli oil	Orange flowers	·05-·1	·870-·880	dextro-rotary	Limonene $C_{10}H_{16}$; linalol $C_{10}H_{18}O$; linalyl acetate $C_{12}H_{20}O_2$; geraniol $C_{10}H_{18}O$; methyl anthranilate $C_6H_4(NH_2)(CO_2CH_3)$.

Nutmeg oil	Myristica fragrans; fruit	8·0-15·0	·868-·915	+14° to +30	Terpenes; myristicol $C_{10}H_{16}O$ (?)
Onion oil	Allium cepa; herb and bulb	·005	1·037	−5	**Allyl-propyl sulphide** $C_6H_{12}S_2$.
Orange oil	Citrus bigaradia (bitter) and citrus aurantium (sweet)	—	·848-·856	+92 to +98°	Limonene $C_{10}H_{16}$; citral $C_{10}H_{16}O$; citronellal $C_{10}H_{18}O$; a crystalline ester melting at 65°.
Orange oil (tangerine)	—	—	·859	+70°	Limonene $C_{10}H_{16}$; citral $C_{10}H_{16}O$.
Origanum oil		See Marjoram Oil.			
Orris oil	Iris species; rhizome	·1 to ·2	—	—	**Irone** $C_{13}H_{20}O$; myristic acid $C_{14}H_{28}O_2$ and its methyl ester; oleic acid $C_{18}H_{34}O_2$; an oleic ester; oleic aldehyde $C_{18}H_{34}O$.
Paracoto oil		1·0-2·0	·925-1·020	0 to +5°	Cadinene $C_{15}H_{24}$; methyl eugenol $C_{11}H_{14}O_2$.
Parsley oil	Petroselinum sativum; seeds	2·0-6·0	1·050-1·100	−5 to −10	**Apiol** $C_{12}H_{14}O_4$; pinene $C_{10}H_{16}$.
Pastinac oil	Pastinaca sativa; fruit	1·5-2·5	·870-·890	*laevo-rotary*	Ethyl alcohol C_2H_6O; octyl propionate $C_8H_{17}.C_3H_5O$; octyl butyrate $C_8H_{17}.C_4H_7O$.
Patchouli oil	Pogostemon patchouli; leaves	2·0-4·0	·975-·995	−50 to −65	Cadinene $C_{15}H_{24}$; patchouli camphor $C_{15}H_{26}O$.
Peucedanum oil	Peucedanum grande; root	traces.	·900	+30 to +35	
Pennyroyal oil	Mentha puelegium; herb	—	·930-·960	+16 to +25°	**Pulegone** $C_{10}H_{16}O$.
Pepper oil	Piper nigrum; fruit	1·0-2·5	·873-·905	−3° to −5	Terpenes; sesquiterpenes.
Peppermint oil	Mentha piperita; herb	·1-1·5	·900-·920	−18 to −33	**Menthol** $C_{10}H_{20}O$; **menthyl acetate** $C_{12}H_{22}O_2$; and numerous other bodies for which see p. 204.
Peppermint oil (Japanese)	Mentha arvensis; herb	—	·895-·905	25° to −43°	
Persea oil	Persia gratissima; leaves	·5	·960	−2	Methyl-chavicol $C_{10}H_{12}O$.
Petit-grain oil	Orange twigs and shoots	—	·885-·900	−2 to +4°	Limonene $C_{10}H_{16}$; linalol $C_{10}H_{18}O$; linalyl acetate $C_{12}H_{20}O_2$; geraniol $C_{10}H_{18}O$; geranyl acetate $C_{12}H_{20}O_2$; sesquiterpene.
Pichurim oil	Nectandra puchury	·5 to 1·0	—	—	Esters of lauric and valerianic acids (?).
Pimento oil (allspice)	Pimenta officinalis; fruit	3·0-4·5	1·040-1·055	−1° to −4°	**Eugenol** $C_{10}H_{12}O_2$; sesquiterpene.
Pimpinella oil	Pimpinella saxifraga; root	—	·960	—	
Pine needle oils	—	(See page 117.)			
Poplar oil	Populus nigra; buds	·3-·6	·900-·905	—	
Ragweed oil	Ambrosia artemisifolia; herb	·1	·870	+26°	
Rose oil	Rosa damascena; flowers	·02	·855-·865 at 30°	+1° to −8°	**Geraniol** $C_{10}H_{18}O$; **citronellol** $C_{10}H_{20}O$; esters; paraffins.

Oil.	Source.	Yield Per Cent.	Specific Gravity.	Optical Rotation.	Constituents.
Rosemary oil	Rosmarinus officinalis; flowering tops	—	·900-·918	+1° to +12°	Borneol $C_{10}H_{18}O$; camphor $C_{10}H_{16}O$; bornyl acetate $C_{12}H_{20}O_2$; cineol $C_{10}H_{18}O$; camphene $C_{10}H_{16}$; pinene $C_{10}H_{16}$.
Rosewood oil	Convolvulus species; wood	—	·900-·910	laevo-rotary	Terpenes.
Rue oil	Ruta graveolens; herb	—	·832-·841	0° to +3°	**Methyl-nonyl-ketone** $C_{11}H_{22}O$; lauric aldehyde $C_{12}H_{24}O$.
Sage oil	Salvia officinalis; leaves	1·0-3·0	·915-·930	+10° to +25°	Pinene $C_{10}H_{16}$; cineol $C_{10}H_{18}O$; borneol $C_{10}H_{18}O$; thujone $C_{10}H_{16}O$; sesquiterpene.
Santal-wood oil (East Indian).	Santalum album; wood	1·5-6·0	·973-·981	−15° to −20°	**Santalol** $C_{15}H_{26}O$; an isomeric alcohol; santalal $C_{15}H_{24}O$; esters.
Santal-wood oil (West Indian).	Amyris balsamifera; wood	—	·950-·964	+10° to +30°	Santalol $C_{15}H_{26}O$ (?).
Santal-wood oil (West Australian).	Santalum cygnorum; wood	—	·945-·965	+5°	Santalol $C_{15}H_{26}O$ (?); esters.
Sassafras oil	Sassafras officinale; wood	3·0-8·0	1·065-1·095	+1° to +4°	**Safrol** $C_{10}H_{10}O_2$; pinene $C_{10}H_{16}$; phellandrene $C_{10}H_{16}$; camphor $C_{10}H_{16}O$; eugenol $C_{10}H_{12}O_2$; cadinene $C_{15}H_{24}$.
Savin oil	Juniperus sabina; twigs	3·0-5·0	·910-·928	+40° to +60°	Pinene $C_{10}H_{16}$; cadinene $C_{15}H_{24}$; sabinol $C_{10}H_{16}O$; ***sabinol actetate*** $C_{12}H_{18}O_2$.
Savory oil	Satureja montana; herb	—	·935-·940	−3°	**Carvacrol** $C_{10}H_{14}O$; pinene $C_{10}H_{16}$ (?); cymene $C_{10}H_{14}$ (?).
Shaddock oil	Citrus decumanum; fruit	—	·860	+90° to +95°	Limonene $C_{10}H_{16}$.
Silaus oil	Silaus pratensis; fruit	1·0-1·5	·980-·990	dextro-rotary	
Snakeroot oil			(See Asarum Oil.)		
Spearmint oil	Mentha viridis; herb	·3-·5	·920-·940	−30° to −50°	**Carvone** $C_{10}H_{14}O$.
Spicewood oil	Laurus benzoin; bark	·43	·923	—	**Methyl salicylate** $C_8H_8O_3$; terpenes.
Spike oil	Lavandula spica; flowers	—	·905-·918	+1° to +7°	Linalol $C_{10}H_{18}O$; cineol $C_{10}H_{18}O$; pinene $C_{10}H_{16}$; camphene $C_{10}H_{16}$; camphor $C_{10}H_{16}O$; borneol $C_{10}H_{18}O$; terpineol $C_{10}H_{18}O$; geraniol $C_{10}H_{18}O$.
Sweet basil oil	Ocymum basilicum; herb	—	·909-·990	+15° to −20°	**Methyl-chavicol** $C_{10}H_{12}O$; linalol $C_{10}H_{18}O$; pinene $C_{10}H_{16}$; camphor $C_{10}H_{16}O$; cineol $C_{10}H_{18}O$.

Tansy oil	**Tanacetum vulgare**; herb	·1-·2	·925-·950	$-25°$ to $-35°$ (English) $+30°$ to $+45°$ (American)	**Thujone** $C_{10}H_{16}O$; borneol $C_{10}H_{18}O$; camphor $C_{10}H_{16}O$.
Tetranthera oil	**Tetranthera citrata**; fruit	5·0	·920	—	Citral $C_{10}H_{16}O$.
Thuja oil	**Thuja occidentalis**; leaves	·5-1·0	·910-·925	$-6°$ to $-14°$	**Thujone** $C_{10}H_{16}O$; fenchone $C_{10}H_{16}O$; pinene $C_{10}H_{16}O$; traces of esters; carvone $C_{10}H_{14}O$.
Thyme oil	Thymus vulgaris; herb	·3-2·5	·900-·950	laevo-rotary	**Thymol** $C_{10}H_{14}O$; carvacrol $C_{10}H_{14}O$; menthone $C_{10}H_{18}$; linalol $C_{10}H_{18}O$; borneol $C_{10}H_{18}O$; cymene $C_{10}H_{14}$; bornyl acetate $C_{12}H_{20}O_2$; pinene $C_{10}H_{16}$.
Turmeric oil	Curcuma longa; root	5·0	·940	dextro-rotary	**Turmerol** $C_{19}H_{28}O$(?); phellandrene $C_{10}H_{16}$.
Turpentine oil (American)	Pinus Australis; wood	—	·855-·870	$+10°$ to $-15°$	**Pinene** $C_{10}H_{16}$; dipentene $C_{10}H_{16}$.
Turpentine oil (French)	Pinus pinaster; wood	—	·855-·870	$-18°$ to $-40°$	**Pinene** $C_{10}H_{16}$.
Turpentine oil (German)	Pinus sylvestris; wood	—	·860-·870	$+15°$ to $+20°$	**Pinene** $C_{10}H_{16}$; sylvestrene $C_{10}H_{16}$.
Turpentine oil (Russian and Swedish)	Pinus ledebourdii; wood	—	·870-·875	to $+20°$	**Sylvestrene** $C_{10}H_{16}$; pinene $C_{10}H_{16}$.
Valerian oil	Valeriana officinalis; root	1·0	·930-·960	$-8°$ to $-15°$	Pinene $C_{10}H_{16}$; camphene $C_{10}H_{16}$; limonene $C_{10}H_{16}$; borneol $C_{10}H_{18}O$ and its esters; terpineol $C_{10}H_{18}O$; a sesquiterpene alcohol $C_{15}H_{26}O$; alcohol $C_{10}H_{20}O_2$.
Valerian oil (Japanese)	Valeriana angustifolia	6·0-7·0	·985-·995	$-8°$ to $-15°$	Pinene $C_{10}H_{16}$; camphene $C_{10}H_{16}$; dipentene $C_{10}H_{16}$; terpineol $C_{10}H_{18}O$; borneol $C_{10}H_{18}O$ and its esters; a sesquiterpene; kessyl acetate $C_{16}H_{26}O_3$.
Verbena oil	Verbena officinalis	—	·890-·900	practically inactive	**Citral** $C_{10}H_{16}O$.
Veti-vert oil	Andropogon muricatus; grass	about 1	1·010-1·030	$+25°$ to $+40°$	
Wintergreen oil	Gaultheria procumbens; leaves	·5-1·0	1·177-1·187	$0°$ to $-1°$	**Methyl salicylate** $C_8H_8O_3$ and traces of other bodies (see page 225).
Wintergreen oil	Betula alba; bark	·5-1·0	1·177-1·187	inactive	
Wormseed oil	*Artemisia maritima*	2·0	·930-·935	—	**Cineol** $C_{10}H_{18}O$; dipentene $C_{10}H_{16}$ (?).
Wormwood oil	Artemisia absinthium; herb	·2-·9	·925-·955	—	**Thujone** $C_{10}H_{16}O$; thujyl alcohol $C_{10}H_{18}O$ and its esters; phellandrene $C_{10}H_{16}$; pinene $C_{10}H_{16}$.
Zedoary oil	**Curcuma zedoaria**; roots	1·0-2·0	·990-1·010	—	Cineol $C_{10}H_{18}O$.

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